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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC, by
STEPHEN LAWROSKI and ASSOCIATES, ARGONNE NATIONAL LABORATORY

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REACTOR FUEL PROCESSING

A REVIEW OF RECENT DEVELOPMENTS

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC,
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Foreword

This quarterly review of reactor fuel processing has been prepared at the request of the U. S. Atomic Energy Commission, Division of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering and Idaho Divisions. Those taking part in the preparation of this issue are J. Barghusen, L. Burris, Jr., P. Fineman, A. A. Jonke, S. Lawroski, W. J. Mecham, D. Paige, J. Royal, W. B. Seefeldt, J. Simmons, R. K. Steunenberg, C. E. Stevenson, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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Section

I

Reactor Fuel Processing

Commercial Aspects of Fuel Processing

Fuel-Processing Plans

In February 1962 the Atomic Energy Commission (AEC) stated that negotiations were still under way with Nuclear Fuel Services, Inc. (NFS) with the objective of developing a satisfactory basis of arrangements for the company to process irradiated fuel from private and government reactors. Considerable progress has been made in the negotiations.[1]

The plant proposed by NFS would be the first privately owned facility of this type in the nation. It would occupy 230 acres within the limits of the 3300-acre Western New York Nuclear Service Center. The plant would include a process building, a fuel receiving basin, a waste-tank farm, a waste burial ground, temporary waste-storage facilities, and a warehouse. The company expects to lease the land from the New York State Atomic Research and Development Authority, which will hold title in the name of the State to the site and the facilities for receiving irradiated nuclear fuel and storing high-level waste. These facilities would be constructed for and operated by NFS.[1]

The AEC's Advisory Committee on Reactor Safeguards considered the NFS plant at a meeting in December 1962. The Committee issued a report in which it stated that "The Committee believes that this plant can be designed and constructed with reasonable assurance that it may be operated without undue hazard to the health and safety of the public."[2] An analysis prepared by the AEC's regulatory staff concerning the safety aspects of the NFS plant was made available to the public through the AEC Division of Licensing and Regulation, Washington.[3] Following these actions, AEC scheduled a public hearing on Mar. 4, 1963, before an atomic safety and licensing board to consider issuance of a construction permit for the plant.[1]

Cost of Perpetual Waste Storage

A report[4] has been issued by S. M. Stoller Associates, New York, on work done under a contract with the New York State Office of Atomic Development to analyze the various elements of technology and cost involved in providing care for high-level, radioactive liquid wastes at the Western New York Nuclear Service Center. It is assumed that these wastes are produced in 15 years of operation of the proposed NFS plant at full capacity.

The purpose of the study was to examine the feasibility of setting up an escrow fund, to be provided by the processing-plant operator during the 15 years that the operator is assumed to be actively engaged at the site. This fund must be sufficient to cover all normal expenses for the care of the waste-storage facility, as well as to provide for replacement of the capital items, essentially for perpetuity.

It was recognized that liquid-waste-storage tanks have a finite lifetime and that the stored wastes would have to be either transferred to new tanks at periodic intervals or processed to permit their permanent disposal in some different manner. For this study it was assumed that the waste-storage tanks at the end of their lifetime would be replaced by essentially identical tanks. As a basis for the study, the waste-tank farm described by NFS in its application to the AEC for a facility license was used.

The assumed waste-tank lifetime has an important effect on the amount of the escrow fund. Since storage of liquid wastes in tanks has only been practiced for about 18 years, the assignment of a tank lifetime for purposes of this study still involved subjective judgment. After examining the available information, it was con-

cluded by the study group that a service life of 50 years is a reasonable assumption. The lifetime of the auxiliary equipment was assumed to be shorter, and therefore the mean life of the entire tank farm was taken as 46 years.

The amount of the escrow fund was established on the basis of current dollars without provision of a factor for escalation. However, the problem of escalation is discussed in the report, and some of the more obvious conclusions are listed.

The total escrow fund was divided into four major subfunds with the following amounts estimated as being required for each:

Annual operating cost fund	$ 800,000
Capital items replacement fund	2,130,000
Contingency fund	1,000,000
Liability insurance fund	1,000,000
Grand total	$4,930,000

The $4,930,000 fund for the perpetual storage of the wastes would require a payment of $246,000 a year by NFS for each of the 15 years of plant operation if one assumes a 4% annuity. Presumably NFS would have to recover this annual payment from its processing-plant customers; this sum would represent about 3% of the total annual cost of the plant and its operation.

The numbers are not intended to be absolute, but rather to give the magnitude of the cost. The report points out that the fund should be adjusted to reflect the actual constructed cost of the waste-storage facility when this is known rather than using the estimated cost.

The report does not translate the annual cost of setting up the escrow fund into a cost per gallon of waste stored. However, in a previous NFS paper, it was estimated that the total annual volume of stored waste generated by the plant[5] would be 100,000 gal. Thus the annual payment of $246,000 to the escrow fund would amount to $2.46 per gallon of waste stored. Since the NFS estimated cost of waste storage, excluding perpetual storage cost, was given as $2.40 per gallon for "standard" waste, the estimated perpetual storage charge would have the effect of doubling the short-term storage cost.

Commercial Waste-Disposal Operations

A second privately owned land waste burial facility has been planned to go into operation at Flemingsburg, Ky.[6] The facility is to be owned and operated by Nuclear Engineering Company of Pleasanton, Calif., which also operates a commercial waste burial facility at Beatty, Nev. It is reported that Nuclear Engineering Company expects to charge its customers, initially, $0.80 per cubic foot for waste burial in approved containers at the Kentucky site. It is also reported that, under terms of its lease agreement with the Kentucky Atomic Energy Authority, Nuclear Engineering Company will pay the State $0.05 per cubic foot of waste buried up to 400,000 cu ft. Thereafter, there will be no additional burial charges by the State until 1 million cu ft of waste has been buried at the 335-acre site. At that point the leasing arrangement will be renegotiated.

Burial of low-level radioactive wastes is also expected to begin this year at the site of the fuels-processing and waste burial facility to be built by NFS in western New York State. Assuming negotiations with the AEC are satisfactorily completed, the waste burial charge by NFS is also expected to be $0.80 per cubic foot in containers approved by the AEC and the Interstate Commerce Commission (ICC).[7]

Availability of Radioisotopes from Spent Fuel

To encourage industry to extract radioisotopes from spent nuclear fuel, the AEC is supporting a study of the availability and cost of separation of radioisotopes contained in spent fuel from both commercial and government-owned reactors. Preliminary estimates indicate that the AEC and the National Aeronautics and Space Administration (NASA) will have to look to commercial reactor operators as the major source of supply of radioisotopes for space power by the early 1970's. The study is being conducted at Hanford, Oak Ridge, and Savannah River. The AEC plans to outline to commercial reactor operators and to commercial fuel processors the net savings that can be obtained by selling the radioisotopes to the AEC instead of discarding them as waste.[8]

In addition to the waste fission products such as Sr^{90} and Ce^{144}, there is considerable interest in the alpha-emitting transuranium isotopes Pu^{238} and Cm^{244}. The latter two are attractive for space auxiliary power units because they

have a long half-life, fairly high specific heat production, and do not emit hard-gamma radiation that requires shielding.

At the present time, Pu^{238} costs roughly $1000 per gram.[9] It is produced from Np^{237}, which is present in spent fuel. Results of a study made at Oak Ridge show that Np^{237} in the first cores from the Dresden and Yankee reactors might amount to 65 and 140 g/metric ton, respectively, at 10,000 Mwd/ton burnup. If burnup reached 40,000 Mwd/ton with the same cores, the neptunium production might reach 695 and 800 g/ton. The results also indicate that the fuel cost savings for each $100 per gram net worth of the neptunium after recovery from spent Dresden and Yankee elements would amount to, respectively, 0.10 and 0.20 mill/kw(e)-hr at 10,000 Mwd/ton.[8]

Processing Fast-Reactor Plutonium Fuels

Processing of fuels from plutonium-fueled fast-breeder reactors was discussed in a paper by Hummel and others of Argonne National Laboratory.[10] The authors state that the development of a substantial power economy based on the use of these reactors will not be limited by technical problems of processing.

The problems raised in processing of plutonium-bearing fast-reactor fuels are largely the same, although of different magnitude, as those in processing fuel from any other high-performance reactor. These problems are radiation damage to reagents, criticality hazards, and waste disposal. Fast reactors generally have higher enrichment fuels that produce much higher specific powers than thermal reactors. Thus the problems of radiation damage and of critical mass are more severe for fast-reactor fuels. The waste-disposal problem, however, is not likely to be significantly different from that for thermal reactors.

The use of plutonium fuels in either fast or thermal reactors should add very little to the cost of processing, since plutonium is present in significant quantity in most spent power-reactor fuels. A kilogram of plutonium is more of a criticality hazard than a kilogram of U^{235}, but there are fewer kilograms in a reactor core of plutonium than in a reactor loading of U^{235}. Thus the hazards during processing are essentially equal.

Fast-reactor fuels could be processed by extensions of present technology; however, increased burnup, alloying ingredients, growth of transuranic elements, and higher enrichment undoubtedly will make processing more costly. Economics, therefore, provides the only incentive to examine advanced processes. The advanced processes being developed fall into two main categories: volatility and pyrometallurgy. Although pyrometallurgical processes may gain their largest economic advantage with metal fuels, they also can handle oxides and probably other compounds. The volatility processes appear to have their largest economic advantage for fuels of low plutonium content, but small-scale work indicates that the processes may be extended to high-content plutonium fuels as well.

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Section

II

Reactor Fuel Processing

Research and Development on Aqueous Processing

Although few novel techniques for the treatment of reactor fuels by aqueous dissolution methods have been disclosed recently, work has continued on the exploitation and refinement of known technology. The principal areas reviewed include fluoride dissolution of zirconium fuel compositions, electrodissolution of various alloys, treatment of carbides, use of amines in extraction, and process instrumentation.

Preparation for Fuel Processing

In order to accomplish the separation of valuable nuclear materials from wastes or scrap material, structural components of fuel elements may be removed mechanically and other components may be dissolved in acid media.

Mechanical Processing Methods

There has been very little mechanical pretreatment work reported recently; however, Oak Ridge National Laboratory (ORNL) has issued a final report[1] on the Sodium Reactor Experiment (SRE) core I dejacketing. This is also included in the Proceedings of the 10th Hot Laboratory and Equipment Conference.

Since the work has been reviewed previously,[2] only some of the conclusions and findings will be mentioned here: (1) The spent SRE NaK-bonded core I fuel was successfully dejacketed mechanically but at a much slower rate than expected. (2) Irradiation under conditions of this reactor experiment had caused unpredicted changes, such as formation of a eutecticlike scale of stainless steel and uranium on the interior surface of the jacket, hardened and/or embrittled jackets, bent and swollen slugs, and badly damaged fuel elements which necessitated dejacketing some of the elements by hand. (3) The dejacketing methods evaluated were too dependent upon the spent fuel remaining unchanged by exposure to reactor environment, storage, or shipping events. (4) More versatile equipment would be required for such fuels as the Fermi blanket or Hallam fuels. (5) The experiment did give some insight into the handling of fuels of this general type.

The report includes a very good tabular résumé of the performance of each unit of equipment, as well as a complete reference list of related work.

Dissolution of Oxide Fuel Cores

From studies of the dissolution of potential breeder-reactor fuels, it was reported by Oak Ridge[3] that the rate at which high-density uranium dioxide–plutonium dioxide pellets dissolve in nitric acid, or in nitric-hydrofluoric acid mixtures, agrees quite closely with values calculated from data observed for uranium dioxide or plutonium dioxide pellets of corresponding theoretical density. Oxidizing agents in nitric acid did not accelerate the dissolution of plutonium dioxide. Kanevskii and others[4] noted that nitric oxide is the principal gas evolved in dissolving uranium dioxide in dilute sulfuric acid containing nitric acid.

Total Dissolution of Metallic Fuels

Studies have continued at the Idaho Chemical Processing Plant (ICPP) on the adaptation of the hydrofluoric acid dissolution process for Zircaloy-clad zirconium-uranium alloy fuels to continuous dissolution. More uranium may be retained in solution as the tetrafluoride by dissolving in dilute (4.8*M*) hydrochloric acid rather than in 10*M* acid. Recently, studies have been made of the continuous oxidation and adjustment of the dissolver solution to provide a noncorrosive aluminum nitrate–zirconium fluo-

ride solution suitable for extraction of uranium.[5] With a 1-min time for mixing the solution obtained by dissolving 3% uranium-zirconium alloy in hydrofluoric acid with complexer solution (1.4*M* aluminum nitrate, 1.7*M* hydrofluoric acid, 0.66*M* nitric acid, and 0.036*M* chromic acid), the uranium was only partially oxidized (43 to 64%) at 46 to 78°C, but was completely oxidized at 94°C, even when the rate of addition of dissolver solution was almost doubled for a brief period (simulating a surge). Other tests indicated that, with aerated solutions, oxidation of uranium occurred rapidly at lower temperatures.

Gens at Oak Ridge[6] has continued previously discussed studies[7] on processes for dissolving zirconium which could be carried out in titanium equipment, since such equipment could also be used for nitric acid and aqua regia processes. A continuous process was demonstrated on the laboratory scale, as shown in Fig. II-1, which is based on a dissolving reagent containing nitric acid, fluoride, about 0.5*M* zirconium, boron, and chromium in both the trivalent and hexavalent states. The mixed reagents are added at a rate needed to maintain the potential of the Cr(III)-Cr(VI) couple at about 1.1 volts to prevent formation of a precipitate. Corrosion is low so long as the ratio of fluoride to zirconium does not exceed a value of about 9. Near this value a zirconium dissolution rate of 20 mg/(cm^2)(min) can be achieved.

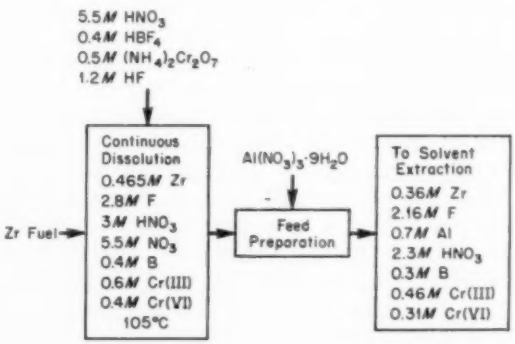

Fig. II-1 Process for dissolving zirconium reactor fuels in Darex titanium equipment.[6]

Electrolytic Dissolution Processes

The application of electrolytic dissolution techniques to the processing of various types of metallic fuels continues to be studied in attempts to develop a broadly applicable process system for nuclear fuels. Aluminum–7.5% uranium alloy was electrolytically dissolved in 1.5*M* to 2.5*M* aluminum nitrate to yield an acid-deficient solution containing aluminum at a concentration[8] of 3.6*M* to 4.2*M*. A small quantity of gray-black particles appeared which dissolved slowly when the solution was heated.

At Savannah River the use of a liquid contact electrolytic dissolver was studied for the removal in nitric acid of stainless-steel cladding from sodium-bonded fuel elements of the Hallam and Fermi reactor types.[9] It was thought that the localized dissolution effected in this type of dissolving would markedly limit the area of sodium, in solid form, exposed to the acid reagent at any one time, and consequently would limit the rate of the reaction.

In early tests, fuel elements were simulated by assembling stainless-steel tubes or rods and filling the annulus with sodium. The effect of fission gases in irradiated fuel was simulated in some tests by pressurizing the annulus with helium. Only mild reactions with sodium were observed if the rods were not pressurized or if the temperature of the acid was held as low as 42 to 46°C. Moderate to violent reactions occurred in hot acid, particularly with helium-pressurized rods and those with larger sodium-filled annuli.

The results of the tests were encouraging in respect to the feasibility of dissolving sodium-bonded fuels by this means, but it was not considered feasible to apply the same technique to NaK-bonded fuels because of their lower melting point.

Separations Processes

Solvent extraction continues to be the principal separation process studied, but some work has been done on precipitation techniques.

Solvent-Extraction Processes

Decontamination and separation of the heavy-metal elements (thorium and elements of greater atomic number) present in aqueous solution are effectively accomplished by extraction with organic solvents. The most-used material for such extraction is tributyl phosphate (TBP), but other compounds are being evaluated as solvents.

Extraction Process Development. The extractability of uranium from solutions resulting from the hydrolysis of uranium carbide has recently been reported from Oak Ridge.[3] In the method studied, impure uranium monocarbide was treated with water for 2 hr at 90°C, following which the product was refluxed with nitric acid to yield a 3*N* acid solution containing about 0.5*M* uranyl nitrate and a waxy residue. The water-washed residue (about 0.3 wt.% of the starting carbide) retained only 0.003% of the uranium and was soluble in acetone.

When the acid solution was extracted with 15% TBP in Adakane diluent, stable emulsions were generated although the uranium loss was only 0.02%. Pretreatment of the feed solution by refluxing with 0.1*M* potassium permanganate (to degrade the organic acids assumed to be responsible for emulsification) yielded a product that did not emulsify upon extraction.

Alternative Solvent Systems. Phosphonates. Blake and others[10] have recently completed a detailed comparison of two dibutylphenyl phosphonates with TBP for extraction of uranium and thorium from spent fuels. The phosphonates were the normal (DBPP) and the secondary butyl (DSBPP) compounds. Because of the limited solubility of their complexes in aliphatic solvents, most tests of these agents were carried out in xylene solution. Both xylene and Amsco 125-82 were used as diluents for TBP. An important consideration in studying the phosphonate reagents was their apparent greater radiation stability as compared with TBP, their compatibility with radiation-stable aromatic diluents, and the probable need for solvent systems that are more radiation stable for the recovery of high-burnup power-reactor fuels.

DSBPP in xylene showed advantages over TBP in the same diluent with respect to greater uranium extractability (1.2 to 1.8 times greater), somewhat better stability to radiation and chemical degradation, a factor of 10 better separation of uranium from thorium, and somewhat better separation of uranium from fission products. TBP in xylene also showed advantages over TBP in Amsco with respect to stability, uranium and plutonium separation, and fission-product separation, although the use of the xylene diluent has the disadvantage that its flash point is considerably lower than that of the Amsco 125-82 diluent. Consideration was given to the use of higher flash point aromatic diluents such as Solvesso-100.

Tertiary Amines. Several of the higher aliphatic amines continue to look quite promising as heavy-metal extractants, and much basic research is being reported on these amines. Baroncelli, Scibona, and Zifferero in two recent articles[11,12] have discussed the complexing from nitrate solutions of plutonium by trilaurylamine and trioctylamine and the complexing of uranium by trilaurylamine. Tetravalent plutonium appears to form a hexanitrato complex in the organic phase, whereas, in the case of hexavalent uranium, several polynitrato complexes appear to be important. Keder[13] has studied the trioctylamine extraction of the actinides from chloride systems and reports that hexachloro, and possibly tetrachloro, complexes of the tetravalent metals are extracted.

Precipitation Processes

Some time ago, preliminary laboratory studies of a dissolution-precipitation-extraction recovery process for Zircaloy-clad zirconium-enriched uranium alloy fuels of the pressurized-water reactor (PWR) seed core type were described.[14] In the process, dissolution would be carried out in hydrofluoric acid, as in the process presently utilized at the ICPP, but there would be added a barium fluozirconate precipitation step (which would remove most of the zirconium and fluoride from solution and would allow a very marked reduction in the volume of liquid waste requiring storage). Also, operation of the solvent-extraction step at a much higher uranium concentration would be permitted, increasing processing capacity. The additional solid waste stream formed would be highly radioactive since most of the strontium, zirconium, and rare earths would be carried in it, but very little uranium would be lost to it. Further laboratory studies have recently been reported which define optimum process conditions more clearly.[15] A process flow sheet is shown in Fig. II-2.*

The process involves precipitation of barium fluozirconate from hydrofluoric acid solution (the dissolver product) by the addition of solid barium nitrate (alone or in combination with

*Figure II-2 is reprinted here by permission from *Industrial and Engineering Chemistry, Process Design and Development*, 2(2): 114 (April 1963).

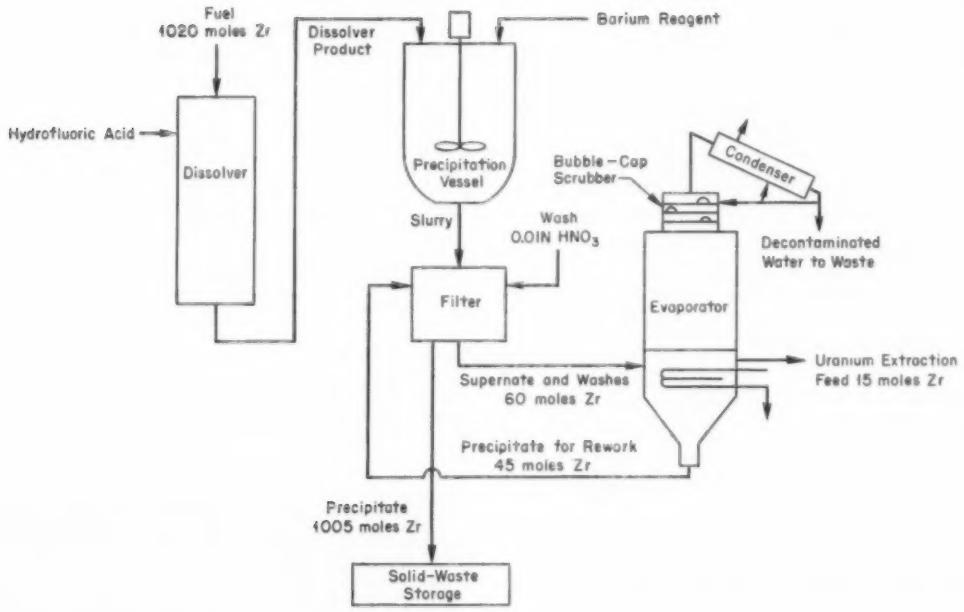

Fig. II-2 Flow sheet for barium fluozirconate head-end treatment for processing of zirconium-uranium fuel.[15]

Table II-1 EFFECT OF PRECIPITATION METHODS ON PROCESS VARIABLES IN BARIUM FLUOZIRCONATE PRECIPITATION*

(Based on PWR Fuel Charge Containing 93 Kg of Zirconium and 1.9 Kg of Uranium)

Method	Dissolver-product volume, liters	Supernatant† from precipitation			Evaporator Products§					
		Volume, liters	Zr, *M*	H^+, *N*	Feed‡ volume, liters	$BaZrF_x$ ppt. for rework, moles	U conc., g/liter	Liquid waste volume, liters¶	$BaZrF_x$ waste, moles	Zr as solid waste, %
Present ICPP process	620						1	1848	0	0
Barium nitrate	510	408	0.1	5.0	1428	1	3.7	510	970	95
Barium hydroxide + barium nitrate	510	408	0.15	1.0	1428	60	19	100	1005	98
Barium fluoride + barium nitrate	620	496	0.1	1.0	1516	45	15	125	1005	98
Barium nitrate–barium fluoride solution	510	1700	0.1	0.3	2720	165	15	125	1005	98

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†Concentrations based on experimental values.

‡Supernatant plus 1020 liters of dilute nitric acid wash.

§Concentrated to approximately 4*N* H^+ for extraction.

¶Same volume as feed to extraction columns.

barium hydroxide or barium fluoride) or by the addition of a solution of barium nitrate and barium fluoride. To obtain 95% removal of zirconium, at least 5 moles of fluoride per mole of zirconium must be present during precipitation. The use of solid precipitants allows maximum reduction in liquid waste volume, but the equipment required needs to be highly resistant to corrosion since varying mixtures of nitric and hydrofluoric acid are present during the precipitation step, which must be carried out at 95°C. Acidity is reduced somewhat by the use of barium hydroxide. The use of barium fluoride as the precipitant allows the employment of dissolver solutions with a low fluoride-to-zirconium mole ratio and a corresponding low acidity. With the barium nitrate–barium fluoride solution, precipitation can be carried out at 23°C, but process volumes are larger. The various precipitation methods are compared in Table II-1.

Process Instrumentation

Dual Conductance Analyzer

The need for in-line instrumentation is basic to all processes considered for modern chemical plant application. Pearson reports[16] on two such instruments for analysis of the dissolver solution that is to be used in the electrolytic dissolution process proposed for the ICPP.

One apparatus (Fig. II-3), described in the April 1963 issue of *Reactor Fuel Processing*,[17] measured the conductance of a solution and of a one-to-one water dilution of that solution. Calibration of the apparatus yielded data shown in Fig. II-4.* Use of the apparatus in a pilot-plant dissolver yielded results that agree with standard chemical analyses with a standard deviation of ±0.2 equivalent per liter for nitric acid and Nichrome solutions over the range of 1.8 to 7.6 and 0.6 to 4.1 equivalents per liter, respectively. In operation, a temperature correction for conductance was used rather than controlling the sample temperature at a constant value.

The second apparatus made use of conductance and density measurements of the dissolver solution and required no dilution. Density was measured semicontinuously by balancing a fixed height of dissolver solution against a column of known density solution (saturated potassium nitrate) and observing its height. A set of calibration curves was developed, and comparison with results of standard chemical analyses gave standard deviations of ±0.18 equivalent per liter of Nichrome solution and ±0.26 equivalent per liter of nitric acid solution.

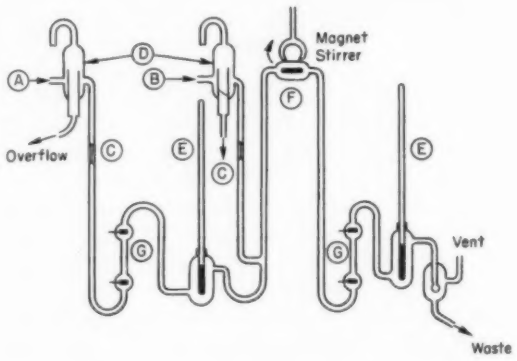

Fig. II-3 Dual conductance analyzer.[16]

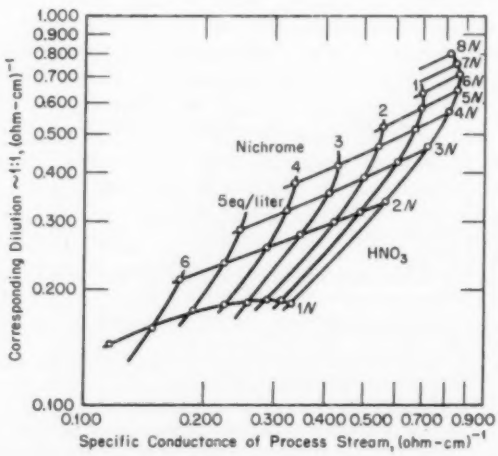

Fig. II-4 Nichrome–HNO_3 calibration data for use with dual conductance analyzer.[16]

*In the preceding issue of *Reactor Fuel Processing* (Vol. 6, No. 2), the in-line conductance analyzer was included as Fig. II-1. Also included was a graph, Fig. II-2, which was erroneously described as the calibration curve for the analyzer. In this issue the diagram of the analyzer (Fig. II-3) is again included, as well as the correct calibration curve for the analyzer (Fig. II-4).

The report concludes that both of the analyzers provided a means of in-line sampling for obtaining control data quickly, as compared with chemical analysis. Since fewer operational difficulties were experienced with the conductance-density device, it was recommended for further development.

Plant and Equipment Design and Operation

Nonconducting Dissolver Basket

Substantial progress was reported[9] toward a practical electrolytic dissolver at Savannah River. The recent work has been along the lines of improving the liquid contact dissolver described in a previous Review.[18]

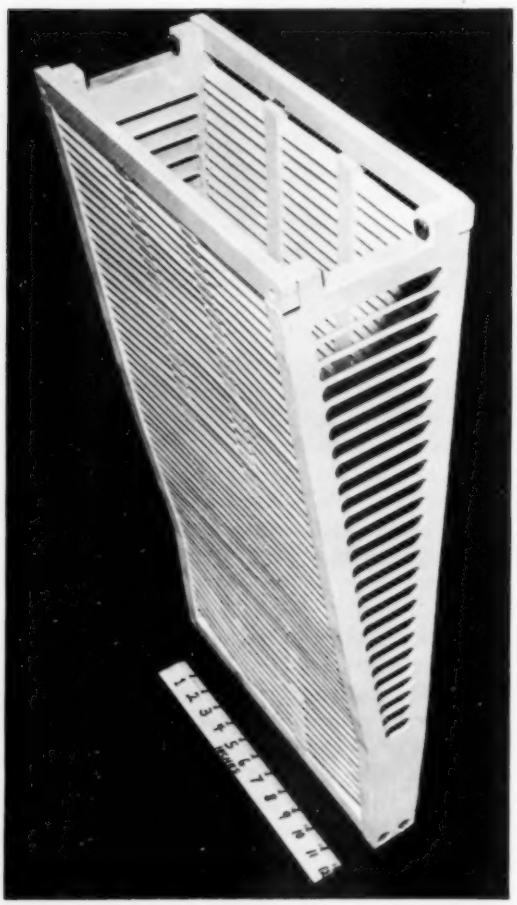

Fig. II-5 Silicone-glass basket.[9]

A nonconducting dissolver basket (for containing the fuel-element charge) made of NEMA Grade G-7 laminate of silicone resin and glass fabric was developed. Samples of this material showed stability after separate exposure to nitric acid and radiation up to 2×10^9 rads. This basket is shown in Fig. II-5. The end panels were shaped from $\frac{3}{4}$-in. sheets of laminate, and the louvers were milled. The side panels, which face the electrodes, were made of $\frac{1}{2}$- by $\frac{3}{16}$-in. strips held in slots in the end panels to give a louvered effect; the panels were joined with tantalum studs.

The basket was exposed to 5.5*M* nitric acid for 64 hr at 85 to 90°C while 100-lb assemblies of stainless steel were being dissolved. The initial weight loss of the basket was 0.1%/hr, but the loss decreased with time. Indicated life of the basket was reported to be 1000 hr, assuming 250 to 300 days cooling of most power fuels. The cost of replacement of the basket would contribute less than 1% to the cost of uranium recovery. A 15% decrease in dissolving capacity was incurred as was expected.

Corrosion and Construction Materials

Most of the power-producing nuclear reactors, which are either in use or proposed, utilize fuel elements that are clad in stainless steel or in a zirconium alloy. Several AEC sites have developed a variety of chemical procedures for the removal of these cladding materials. Two of the most promising procedures are the Sulfex process, for the decladding of stainless-steel fuels, and the Zirflex process, for the decladding of zirconium or zirconium alloy clad fuels. Chemical decladding is done for the former in boiling 4*M* sulfuric acid and for the latter in boiling ammonium fluoride–ammonium nitrate. In preceding issues of *Reactor Fuel Processing*,[19–21] corrosion information essential to the practical development of such processes was presented.

The interests of the various sites have influenced the selection of construction materials for these processes. The need for a construction material compatible with Sulfex, Zirflex, and Niflex processes led Hanford to

develop a new high-nickel alloy, HAPO-20. ORNL did not include the Niflex process in its considerations, and, as a result, chose Nionel. Idaho's acceptance of the Sulfex decladding procedure was based on process compatibility with their existing Carpenter-20Cb dissolution equipment. Savannah River and ORNL have facilities made of stainless-steel type 309SCb, and both are interested in determining the compatibility of Zirflex process-

Table II-2 CORROSION OF WELDED AND UNWELDED NIONEL IN REFLUXING SULFEX ENVIRONMENTS[22]

Material	Corrosion rate, mils/year		
	$4M$ H_2SO_4	$4M$ H_2SO_4 plus 25 g of stainless-steel type 348 per liter	$6M$ H_2SO_4
Nionel, wrought			
Updraft condenser	25	6	130*
Cold-finger condenser	42		
Solution air-sparged	23		
Nionel, welded			
Metal-arc-welded $\frac{1}{4}$-in. plate	13	21	60*
Inert-gas-welded $\frac{1}{4}$-in. plate	15	8	90*
Metal-arc-welded $\frac{1}{2}$-in. plate	16	9	
Inert-gas-welded $\frac{1}{2}$-in. plate	20	5	
Nionel, wrought (nonisothermal: specimen at a higher temperature than solution)	32	20	

*Corrosion rate after more than 400 hr of exposure; rate increasing with time owing to intergranular attack.

rangements vs. air sparging of boiling solution, the effect of dissolved stainless steel, sulfuric acid concentration ($4M$ vs. $6M$ sulfuric acid), welded vs. nonwelded specimens, and the effect of maintaining metallic surfaces at temperatures above that of the solution (characteristic of heat-transfer surfaces). Small variations in corrosion rate were obtained in 240-hr exposures for the runs performed in triplicate. Results were independent of the type of acid

ing procedures with such equipment. There are some discrepancies between the corrosion data obtained at the several sites; for instance, complete agreement was not achieved on the effect of dissolved stainless steel in Sulfex solutions on the corrosion of Nionel. In a recent report originating at Brookhaven National Laboratory, additional data on the Sulfex and Zirflex process systems are presented, and it is hoped that this will clarify, at least in part, some of the past discrepancies.[22] Katz and Isler examined Nionel and Carpenter-20Cb in both Sulfex decladding and nitric acid dissolution environments. In addition, several brief tests were made with stainless-steel type 309SCb in Sulfex environments. The largest number of test parameters were applied to Nionel in Sulfex. These include the variation in corrosion in triplicate runs with wrought Nionel, the effect of sulfuric acid grade, updraft and cold-finger condenser ar-

used (technical grade vs. chemically pure sulfuric acid).

Typical results gathered from the many tables in the report are shown in Table II-2. Tests were run in multiples of 48-hr periods except in those tests which were carried out in the presence of dissolving metal, where the period was determined by the dissolution time. Solutions were renewed at the end of each test period. Liquid-phase specimens were supported in glass baskets and were fully immersed in the liquid phase. Vapor-phase specimens were suspended above the solution and were at least partially wetted by condensate.

In earlier work at other sites, it had been found that corrosion rates were often dependent on the type of condenser system used. Similar observations were made in the Brookhaven study. When an updraft condenser was used or when the boiling solutions were sparged with air, the observed corrosion rates in $4M$ sul-

furic acid were about 25 mils/year. When a cold-finger type of condenser was used, the corrosion rate nearly doubled. The cold-finger condenser is thought to retain a greater quantity of the decomposition gases in solution, thus influencing the result obtained.

The presence of dissolved stainless steel lowered the corrosion rate by a factor of 4 to 10, depending on the source of the dissolution product. Twenty-five grams of stainless-steel type 348 per liter reduced the rate to 6 mils/year while the same concentration of stainless-steel type 304 reduced corrosion to 0.8 mil/year. The effect appeared to be independent of the concentration of dissolved stainless steel in the range of 5 to 50 g/liter. In actual dissolution tests varying in time from 4.9 to 9.5 hr, the average corrosion rate was 13 mils/year. This is less than that obtained from corrosion-product-free solution but greater than that which would be expected from tests containing only dissolved stainless steel. These unexpected results possibly reflect the shorter test periods.

The welded specimens of Nionel subjected to the Sulfex environments were of three types: welded $\frac{1}{4}$-in.-thick plate, welded $\frac{1}{2}$-in.-thick plate, and welded $\frac{1}{2}$-in.-thick plate containing cross welds. Two different types of welding procedures were employed: metal arc and inert gas. Corrosion rates of welded specimens were approximately one-half as much as those observed in the unwelded counterparts. However, the presence of dissolved stainless steel in the acid did not reduce the rates of attack to the same degree as was observed in tests containing unwelded specimens. The differences observed between the three weld types were small.

Initial tests of Nionel in 6*M* sulfuric acid were run for 240-hr periods and showed liquid-phase corrosion rates of 30 to 40 mils/year for both wrought and welded specimens. However, later tests run for longer periods indicated sharply increasing corrosion rates attributable to intergranular attack. The rapid increase in rates on welded specimens occurred between 240 and 430 hr of exposure. Wrought specimens were not affected until about 1000 hr. Visual examination of these specimens showed severe intergranular attack of the base metal with no visible attack of the weld evident. In two 240-hr tests, the presence of 25 g of dissolved stainless steel per liter had no effect on the corrosion rate. It is evident that, on the basis of these results, Nionel is not a suitable construction material if 6*M* sulfuric acid is to be employed for decladding.

Several nonisothermal tests were made with Nionel and refluxing 4*M* sulfuric acid in order to determine whether Nionel would be a suitable material for heat-transfer surfaces, such as heating coils or steam jackets. The corrosion rate was 32 mils/year and was found to be independent of surface temperature up to 300°F (149°C). The addition of 25 g of dissolved stainless steel per liter to the environment had the effect of reducing the corrosion rate by a factor of 2.

Tests were also made to determine whether Nionel would be compatible with nitric acid core dissolvent, and selected data are presented in Table II-3. (It was presumed that the bulk of the power-reactor fuels would consist of nitric acid–soluble uranium dioxide.) Nitric acid concentrations used in the tests included 5*M*, 8*M*, and 10*M*. In the latter two solutions, there was a rapidly increasing corrosion rate of specimens in the vapor phase due to severe intergranular attack. In the case of welded coupons, there was preferential attack of the base metal. The buildup of corrosion products in the solution which resulted from high vapor-phase attack caused, in turn, an accelerated corrosion rate in the liquid phase.

Results in 5*M* nitric acid were less severe. However, there was still considerable evidence of intergranular attack in the vapor phase, with corrosion rates reaching 40 to 50 mils/year after 1800 hr. Welded specimens were attacked more severely than were wrought specimens. In other tests with 5*M* nitric acid, vapor-phase attack appeared to be eliminated by holding the liquid temperature at 90°C. The authors suggest that the use of Nionel in nitric acid systems be limited to below-boiling-point temperatures, preferably below 90°C. If the liquid-phase corrosion data[22] for refluxing 5*M* nitric acid is examined closely, it is clear that its rate also increases gradually with exposure time. During the 1800 hr of the test, the rate of attack varied as the 0.45 power of time. Extrapolation to 100,000-hr exposure time indicates that the rate would rise to approximately 18 mils/year, which would still be acceptable.

Carpenter-20Cb was also tested, but less extensively, as an alternative construction material for the Sulfex process. In boiling 4*M* sulfuric acid, the corrosion rates observed were

very similar to those observed for Nionel. However, welded specimens corroded at almost double the rate of wrought specimens. Dissolved stainless steel lowered the corrosion rate of Carpenter-20Cb by about the same amount as it lowered the corrosion rate of Nionel.

Nitric acid core dissolvent (4*M* and 10*M*) corroded Carpenter-20 at rates comparable to that of Nionel. However, the corrosion rates for inert-gas-welded specimens were higher by a factor of 5 to 10, and those for fusion-welded specimens were so high as to be completely unsatisfactory. Because of the generally poor performance of Carpenter-20Cb welds, particularly in nitric acid, and since the vapor-phase corrosion problem appeared to be no less serious than with Nionel, testing was not extensive.

Zirflex Corrosion Studies

Three alloys were examined for possible application in Zirflex processes: stainless-steel types 309SCb and 304L and Nionel.[22] None of these alloys was found to be satisfactory for use with noninhibited Zirflex solutions: 6*M* ammonium fluoride and 0.5*M* ammonium nitrate. Corrosion rates in the noninhibited solutions were 150, 300, and 250 mils/year, respectively.

The effect of adding cupric nitrate to the extent of 0.01*M* and 0.1*M* was examined to determine possible inhibition properties. The inhibiting effect was most pronounced for stainless-steel type 309SCb; the reduction in corrosion rate when 0.01*M* cupric nitrate was added was a factor of 4 to 5. However, copper was slowly lost from these solutions by plating out on stainless-steel surfaces, particularly at weld locations. The loss is slow enough so that additions during a dissolution should not be necessary. The loss of cupric ion due to plating was more rapid for stainless-steel type 304L and Nionel. Recommendations regarding the use of these alloys in Zirflex systems were not made by the authors in the report. In a private communication of June 6, 1963, General Electric stated that "corrosion rates ... are markedly reduced during actual dissolution of zirconium due to increased *p*H (from NH_3 production) and reduced free fluoride concentration."

Zirconium Dissolution in Titanium Equipment

The Darex process is under serious consideration as a means of decladding stainless-steel-clad fuels. The eminently satisfactory construction material for this process is titanium. With the strong incentive existing for multipurpose use of dissolution equipment, Oak Ridge has been examining a process for decladding zirconium-clad fuels which also would be compatible with titanium dissolution equipment. Progress in the efforts to develop a

Table II-3 CORROSION* OF NIONEL IN REFLUXING CORE DISSOLUTION ENVIRONMENTS[22]

(Corrosion Rate: Mils/Year)

Material	Exposure time, hr	5*M* HNO_3		8*M* HNO_3		10*M* HNO_3	
		Liquid	Vapor	Liquid	Vapor	Liquid	Vapor
Nionel	240			3	2	317	655
	480			35	65		
Nionel, metal-arc-welded	240	1.3	0.7			13	133
	480	3.6	2.9				
	1680	4.8	24				
Nionel, inert-gas-welded	240	0.8	0.7			348	688
	480	1.8	2.0				
	1968	4.4	43				
Nionel (nonisothermal)							
Specimen temp.							
226 to 240°F (108 to 116°C)	240 to 768	3 to 22				*	
250 to 300°F (121 to 149°C)		24 to 380†				185 to 1430‡	

*High corrosion rates and increases of rates with time are associated with intergranular attack.
†Exposure time: 240 to 678 hr.
‡Exposure time: 240 hr.

compatible zirconium-dissolution process has been reported previously in *Reactor Fuel Processing*.[19,23] A laboratory demonstration of one such flow sheet (Fig. II-1) has been reported recently.[6,24] The dissolution medium used was 3*M* nitric acid–1.2*M* hydrofluoric acid–0.4*M* fluoboric acid–0.6*M* Cr^{3+}–0.4*M* Cr^{6+}–0.46*M* zirconium. The alloy dissolved was 2% uranium in zirconium. Dissolution rates and corrosion rates were monitored during this demonstration. As previously reported[19] the concentration of chromium ions in the dissolvent is critical in relation to the titanium corrosion rate. Fresh reagent was added during the dissolution at a rate determined by the potential of the Cr^{3+}-Cr^{6+} couple in the dissolver effluent.

The success of the use of titanium in this system is also predicated on proper pretreatment for the development of a satisfactory protective film on the titanium. Prior to the laboratory demonstration, the lower portion of the dissolver was pretreated five times by alternate cycles of boiling solution (10 min) and an air stream (until dry). It is thought that the protective film that develops is probably a mixed zirconium-titanium fluoride or oxyfluoride. Chemical analysis of scraped-off film yielded the following results: 28.6 wt.% fluoride, 49.7 wt.% zirconium, and 0.45 wt.% titanium. The X-ray pattern matched quite well the pattern of $ZrOF_2$, but the composition of the film is still considered uncertain. The upper portion of the vessel, which was exposed only to the vapor phase, was not given this pretreatment, because preliminary corrosion tests had indicated that rates of attack in the vapor phase were very low and that during dissolution a coat forms which probably protects the titanium. However, examination of the vessel after 40- to 50-hr dissolution experiments were completed revealed many pits (100 mils deep) in areas where the vessel had not been pretreated. Thus it appears that pretreatment of the entire vessel is necessary. One possible cause of vapor-phase pitting may have been that, in some early runs, fresh reagent added to the vessel was allowed to trickle down the vessel wall. In later runs the reagent was introduced in such a way that it fell directly into the dissolvent without contacting the walls.

To gain some understanding of the nature of the protective film, the corrosion beneath the film, and the methods of producing the film, a group of nine welded samples of Ti^{60} were immersed in boiling dissolvent, removed periodically, air dried, and weighed. Without intervening periods of air drying, the corrosion rate of titanium would be expected to be about 400 mils/month. The first 10 immersions were each for periods of 10 min. The eleventh was for 30 min, and the twelfth, thirteenth, and fourteenth were each for a period of 1 hr. The specimens lost weight rapidly for the first 10 min, less rapidly for the second and third exposures, and gained weight during all subsequent exposures. These results show the beneficial effect of the air exposure in producing the protective oxide coat. The average corrosion rate was 10 mils/month over the entire exposure period. Since exposure to air is necessary to achieve protection, periodic interruption of the continuous dissolution process would be necessary to replenish the oxide-containing film.

Several tests were also made to determine whether the corrosion of treated and untreated Ti^{60} is influenced by contact with dissolving Zircaloy-2 alloy. Little effect was observed in a 2-hr continuous dissolution experiment at the boiling point. Untreated titanium corroded at rates of 1 to 2 in. per month, whereas the pretreated titanium specimen showed only a small weight gain.

Further studies of the corrosion characteristics of titanium in this process are thought necessary to clarify its behavior for possible application to this processing system.

As was stated earlier in this section, the ICPP processes (among other fuels) enriched-uranium–Zircaloy fuels. It has concerned itself with (1) increasing overall plant capacity for the latter fuels and (2) adapting the existing equipment to handling fuels containing quantities of uranium greater than 1% (up to 2 or 3%). To achieve the first objective, it has been proposed to substitute a continuous dissolver for the existing batch dissolver. Achievement of the second objective would require some changes in the flow sheet as now used. The present flow sheet utilizes a solvent of 10*M* hydrofluoric acid, which is capable of homogeneously dissolving zirconium alloy fuels containing up to 1% uranium. The capability of homogeneous dissolution does not apply if the uranium content exceeds this value. It has been determined in laboratory studies that, when a so-called "dilute" flow sheet is used (4.8*M*

hydrofluoric acid), perhaps supplemented by additions of small quantities of oxidants, fuels containing 2 to 3% uranium can be homogeneously dissolved. The first of a proposed set of three reports describing developments in this area has been published.[25] Miniature continuous dissolving equipment together with corrosion sample pots, for the evaluation of Monel and Carpenter-20Cb as construction materials, were operated in the laboratory. Figure II-6 is a schematic diagram of the equipment and the flow streams. Corrosion evaluations were made of the equipment and of samples contained in the two corrosion sample pots.

Partial results are shown in Table II-4. Both Monel and Carpenter-20Cb appear to be satisfactory in 10*M* HF containing hydrogen peroxide; however, contact with the dissolver feed at the inlet resulted in deep longitudinal grooves in the Carpenter-20Cb dissolver tube. This attack was not observed in those solutions containing copper chloride and manganese chloride. The latter compounds were added in some tests in an effort to catalyze the peroxide oxidation of the U(IV) to U(VI).

Neither alloy is satisfactorily resistant to 10*M* HF containing 0.6*M* nitric acid. The Carpenter-20Cb corrosion pot suffered a nozzle failure in 68.5 hr; this corresponds to a corrosion rate of 720 mils/month. In addition, this material suffered catastrophic attack in the dissolver feed solution. The more dilute dissolvent, 4.8*M* hydrofluoric acid – 0.03*M* nitric acid, was less corrosive to the two alloys.

Monel was totally unsatisfactory in the dilute hydrofluoric acid containing 0.55*M* aluminum nitrate. The presence of weld-stress cracks in the Carpenter-20Cb dissolver tube for this experiment indicates that this alloy also would be unsatisfactory for extended use.

In general, Monel, which can be satisfactorily field-welded, may be preferred over Carpenter-20Cb because of the possibility that the latter may not be adequately annealed in the field and may fail at sensitized areas in or adjacent to welds.

Cathodic Shield

The Savannah River Laboratory has been investigating an electrolytic dissolution technique for both stainless-steel- and zirconium-matrix fuels (see discussion under the heading "Plant and Equipment Design and Operation" in this section). This development has progressed to the point where a pilot-plant-sized dissolver has been constructed and is being used

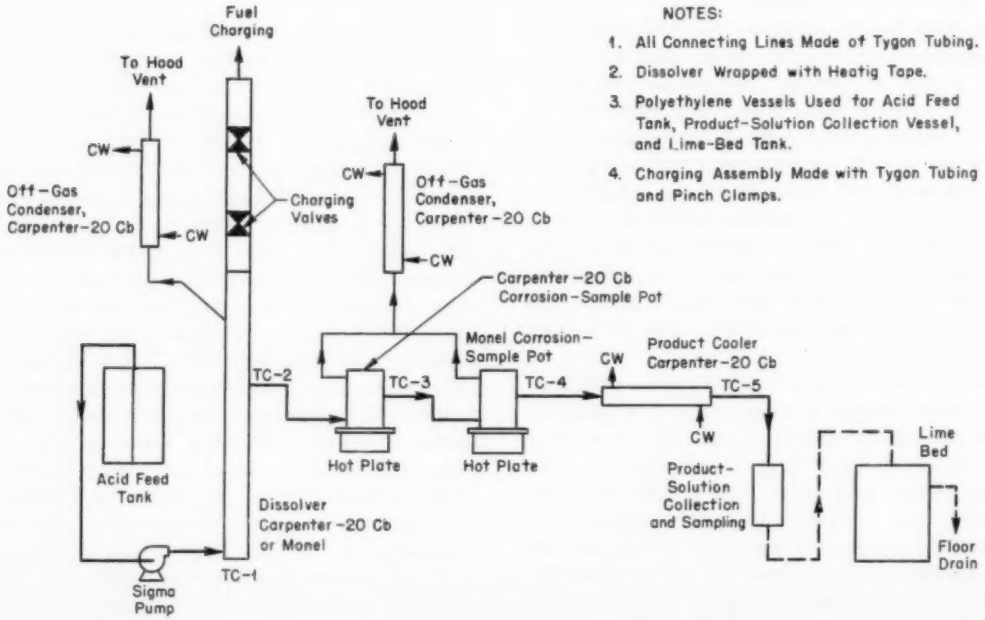

Fig. II-6 Miniature zirconium dissolver equipment, flow diagram.[25]

Table II-4 CORROSION OF MONEL AND CARPENTER-20Cb IN PROPOSED ZIRCONIUM FUEL DISSOLVENT[25]

(Temperatures: 140 to 200°F; Continuous Flow of Dissolvent)

Dissolvent	Dissolver material	Corrosion rate, mils/month			
		Dissolver		Corrosion pots*	
		Tube	Inlet coupon	Monel	Carpenter-20Cb
10*M* HF–0.03*M* H_2O_2	Carpenter-20Cb	Local attack; deep grooves	4.1†	1‡	0.3‡
10*M* HF–0.60*M* HNO_3	Carpenter-20Cb	1180	335†	5 to 20‡	13 to 80‡
10*M* HF–0.03*M* H_2O_2–0.001*M* $CuCl_2$–0.001*M* $MnCl_2$	Monel	Resistant	7.2	Resistant	Resistant
10*M* HF (aerated)	Carpenter-20Cb	Resistant	0.2†	0.3 to 9‡	0.1 to 0.7‡
4.8*M* HF–0.03*M* HNO_3	Carpenter-20Cb	Resistant		1.3 to 5.3‡	0.7 to 2.8‡
4.2*M* HF–0.55*M* $Al(NO_3)_3$	Carpenter-20Cb	Weld-stress cracks	7.4	800	Resistant

*Values include corrosion rates in both liquid and vapor phases.
†Coupon sensitized.
‡Coupons inserted in pots.

for experimental investigations. The current progress report from Savannah[9] describes a nonconducting dissolver basket (Fig. II-5) that has been fabricated from a silicone resin and glass fabric laminate.

Following the installation and operation of the silicone-glass basket, very slow localized anodic corrosion of the dissolver vessel was noted. The rate of attack was about 100 mils/year and was limited to an area behind the cathode, particularly on the tank bottom. This corrosion was traced to current leakage from an anodic stainless-steel surface, to the tank bottom, and back to the cathode. Several experiments were performed in order to determine how stray current corrosion could be avoided. A new cathodic shield was constructed (see Fig. II-7) to prevent anodic corrosion of the dissolver tank.[9] It was reported that the shield decreased the rate of corrosion in the attacked area from 100 mils/year to less than 0.5 mil/year.

Construction Materials for Transuranium-Element Separation Facility

At ORNL, plans are progressing for the isolation and recovery of transuranium elements. The process presently envisioned makes use of concentrated chloride solutions covering a wide range of acidities. In some process steps, nitrate will also be present. In solutions containing appreciable concentrations of the transuranium elements, peroxide is expected to be present as a product of the radiolysis of the water. Plans are progressing for the construction of process equipment, and material take-offs are now being made. The flow sheets, at present, assume that Hastelloy C corrosion rates of less than 3 mils/month for service in the separations systems and less than 1 mil/month in storage tanks will be acceptable. Feed adjustment tanks, including the vessel head and all dip tubes, will be tantalum lined.[26] Product storage tanks will probably be tantalum-lined Hastelloy C vessels with Zircaloy tops and dip tubes. Zircaloy may be desirable for many applications where corrosion rates for Hastelloy C are borderline since, in general, the corrosion rate of Zircaloy is one-tenth that for Hastelloy C. Fabrication problems and costs of both materials may be restrictive and are under investigation. The requirement for the special heat-treatment of Hastelloy C after welding places severe limitations on fabrication techniques.

Corrosion testing is continuing for a number of proposed construction materials for components in the transuranium separation facility.

The materials include[26] Hastelloys B and C, niobium, tantalum, titanium, and Zircaloy-2. Table II-5 shows the corrosion rates of Hastelloy B and Hastelloy C in a number of simulated process environments. It is evident that in most cases Hastelloy B exhibits a resistance that is superior to that of Hastelloy C. In the first three solutions, Hastelloy C specimens were susceptible to preferential attack in heat-affected zones adjacent to welds, with observed penetrations ranging up to 30 mils. The use of a postweld heat-treatment at 1227°C eliminated the attack of heat-affected zones without affecting the general corrosion resistance of the alloy. The only environment that produced heat-affected attack in Hastelloy B was the boiling lithium chloride–hydrochloric acid solution. The tests in the last two environments shown in the table were made as a result of concern over the effect of corrosion-product iron building up in process solutions. Corrosion rates of both alloys were a factor of 2 to 3 higher in the presence of 200 ppm ferric iron; there was a slight increase in corrosion rate with time of exposure.

Table II-5 CORROSION OF WELDED HASTELLOY B AND HASTELLOY C BY SIMULATED TRANSURANIUM SOLUTIONS[26]

(Exposure Time: 1000 Hr)

Solution	Temp., °C	Penetration rate, mils/month			
		Hastelloy B		Hastelloy C	
		Solution	Vapor	Solution	Vapor
3*M* HCl–O_2	43	5.1	4.3	19.4*	5.0*
10*M* LiCl–0.1*M* HCl–O_2	130	1.8	2.3	22.0	40.2
10*M* HCl–0.0023*M* $LaCl_3$–H_2O_2	35	5.7	4.9	5.9	5.4
6*M* HCl	43	5.3†	6.8†	10.2*	6.5*
6*M* HCl–200 ppm Fe^{3+}	43	17.5†	7.2†	22.9*	8.5*

*400-hr exposure.
†300-hr exposure.

Fig. II-7 Cathodic shield.[9]

Niobium was exposed to several chloride-containing solutions to determine its sensitivity to hydrogen embrittlement. A solution-exposed specimen cracked during bending after 1000 hr at 105°C in oxygenated 6*M* HCl solution. The hydrogen content of the specimen was 530 ppm, compared with 4 ppm in the unexposed material. There was little effect on the general corrosion rate. Similar but less severe fractures occurred in 10*M* lithium chloride–0.5*M* HCl solution. The use of platinum tack welded to niobium failed to prevent embrittlement of the niobium, although some reduction in the amount of hydrogen pickup was obtained. Tantalum was completely resistant to attack in all environments tested. Some evidence of hydrogen pickup was observed in hot 6*M* HCl solution when

tantalum was exposed in contact with aluminum, but this effect appeared to be minor in character. No test specimens exhibited cracking during a bend test.

Titanium is attacked in a catastrophic manner in hot hydrochloric acid solutions. However, the addition of a strong oxidant such as nitric acid produces considerable improvement in resistance. For example, after 96 hr at 105°C in $6M$ HCl–$10M$ HNO_3 solution, the attack on an immersed titanium specimen was 3 mils/month. Addition of hydrogen peroxide to a concentration of $0.001M$ did not have the same inhibiting effect. The corrosion of Zircaloy-2 in chloride environments, either with or without oxidants, was of the order of 0.3 mil/month. The susceptibility of Zircaloy-2 to hydrogen pickup appeared to be negligible.

Corrosion of Stainless Steel in HNO_3-HF-U-Graphite Environment

In conjunction with the development of processes for handling graphite-containing fuels, welded specimens of types 304L and 347 stainless steels were exposed to refluxing $2M$ nitric acid–$1M$ hydrofluoric acid containing 50 g of uranium per liter (as nitrate) and 20 g of crushed graphite per liter. Measured corrosion rates of types 304L and 347 stainless steels were 3.9 and 4.6 mils/month, respectively, for 48-hr exposures. Vapor-phase corrosion was about 0.1 mil/month for both alloys. There was no indication of local attack on any specimen, but the overall rates for interface and solution specimens of type 347 were higher by factors of 3 to 9 than those obtained in similar tests in the absence of the graphite and uranyl ion.[23]

Cracking of Stainless Steel by Sodium Hydroxide Trapped in Equipment

The effect of various ions on the speed of sodium hydroxide cracking of stainless steels is being examined at Hanford.[27] The effect of the presence of potassium permanganate and its reduction products was studied because of the usage of 18% NaOH–3% $KMnO_4$ in the decontamination of PRTR. Since concern is not about generalized corrosion in areas where solutions circulate readily, but rather about cracking which occurs as a result of residual chemicals trapped in equipment, tests involving crevices were employed. Each sample consisted of a $\frac{3}{8}$-in. flared tubing connector made of type 316 stainless steel, with a short flared piece of type 304 stainless-steel tubing in place. The connectors were assembled while submerged in the decontaminating solution or in sodium hydroxide solution, removed, wiped on the outside, tightened, and dried at 110°C for 2 hr. They were then exposed to steam at 275°C for varying periods of time, disassembled, and examined for cracks. Control samples not exposed to the decontaminating solutions were included. The sodium hydroxide samples cracked through the stressed portion of the nut in 3 to 20 hr at temperature. Of six fittings exposed to the decontaminating solution, only four showed minor cracks in the flared tubing after 150 hr. Tests with other concentrations of permanganate are being made, and metallographic sections of the cracks are being prepared.[27]

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Section

III

Reactor Fuel Processing

Research and Development on Nonaqueous Processing

Volatility Processes

Fused-Salt Volatility Process

Fused-Salt Fluoride-Volatility Pilot-Plant Decontamination Runs. The Oak Ridge National Laboratory (ORNL) Fluoride-Volatility Pilot Plant was modified in 1959 and 1960 to process zirconium-uranium alloy fuel elements. The principal modification was the addition of hydrogen fluoride dissolution, or head-end, equipment to the Aircraft Reactor Experiment Pilot Plant facility. Dissolution of the fuel elements is performed with anhydrous hydrogen fluoride in a molten salt of equimolar sodium fluoride–lithium fluoride containing 24 to 45 mole % zirconium tetrafluoride at 650 to 500°C. The zirconium-uranium alloy is thereby converted to zirconium tetrafluoride and uranium tetrafluoride, both of which are soluble in the fluoride salt. Submicron-size solids generated during the dissolution are removed from the off-gas by a technique of continuous washing with liquid hydrogen fluoride. After dissolution the uranium is decontaminated from fission products by conversion to volatile uranium hexafluoride with elemental fluorine at 500°C. Further decontamination of the uranium hexafluoride from trace fission products is accomplished by an absorption-desorption cycle on a sodium fluoride absorber at 100 and 400°C. Product uranium hexafluoride is collected in cold traps.

Six processing runs on 5.2- and 6.5-year-decayed zirconium-uranium Zircaloy-clad fuel elements have recently been completed in the ORNL Fluoride-Volatility Pilot Plant.[1] Previously, two series of runs using nonirradiated fuel had been performed in the pilot plant to evaluate equipment performance (T series) and to demonstrate the flow sheet (TU series). The principal objectives of runs using irradiated fuel were to study uranium decontamination from fission products and to investigate general fission-product behavior in the plant.

Descriptions of the pilot plant and previous run series (including the first four runs of the R series) were presented in the January 1963 issue of *Reactor Fuel Processing*.[2] The present report presents further data, principally concerning specific fission products (antimony, niobium, ruthenium, technetium, and molybdenum) which form volatile fluorides.

Decontamination factors for ruthenium and niobium obtained in the dissolution step appear consistent with earlier work on a smaller scale with two- to three-year-cooled fuel.[3] The mechanism of ruthenium removal was believed to be primarily adsorption on dissolver surfaces, whereas niobium removal was probably by volatilization. The decontamination factors for ruthenium, niobium, and antimony in the present series of pilot-plant runs are given in Table III-1. The mechanism of Sb^{125} removal is believed to be similar to that of Nb^{95}.

Transfer of activity to the dissolver off-gas stream was also monitored. As is stated earlier, this off-gas stream is scrubbed with liquid hydrogen fluoride to remove entrained solids, which are collected and discharged with waste hydrogen fluoride to a caustic neutralizer. Only a small fraction of the volatile fission-product activity removed from the salt during dissolution reached the waste hydrogen fluoride system. The in-process holdup of activity was attributed to plating-out of fission products on dissolver surfaces or to condensation at cooler regions of the dissolver or off-gas system. Transfer of Cs^{137}, uranium, gross β, and gross γ activity to the waste hydrogen fluoride system was negligible. Of the three volatile fission products considered, only Sb^{125} showed consistent and appreciable volatilization or entrainment.

Table III-1 DISSOLUTION DECONTAMINATION FACTORS[1]

(Based on Calculated Feed Activity and Fluorinator Salt Samples)

Nuclide	Approximate decontamination factors*					
	R-1	R-2	R-3	R-4	R-5	R-6
Sb^{125}	4	>5	8	10	>100	16
Ru^{106}	>100	>58	1	30	6	7
Nb^{95}	30	20	1	300	75	30

*Calculated activities assume no specific fission-product decay prior to fuel discharge from the reactor.

In this series of hot runs, major increases in the product cation impurity level were noted in runs R-5 and R-6, continuing the trend of run R-4 (Table III-2). In runs R-5 and R-6, volatile fluorides (molybdenum, technetium, and neptunium) accounted for most of the contamination. Molybdenum, technetium, and neptunium fluorides were earlier found to absorb and desorb from sodium fluoride with uranium hexafluoride.[2] The increase in fission-product concentration in the uranium hexafluoride was attributed partly to an excessive flow of purge gas which resulted from a leaking flange and partly to the nonoptimum operation of the sodium fluoride absorber bed.

During fluorination the volatile fission products (with the probable exception of tellurium and iodine fluorides) complex to some extent with the sodium fluoride in the lower zones of the absorber.[2] The lowest portions of the absorber bed are displaced into the waste salt by piston action. During the present runs, approximately 10% of the total sodium fluoride bed was discharged in this manner in each run. This operation moves the fission-product band on the sodium fluoride absorber bed downward with respect to the absorber wall. After fluorination, when the upper zones of the absorber bed are heated to 400°C for desorption of uranium hexafluoride, the fission products migrate upward in the bed by a mechanism that is similar to the one that occurs in chromatography. If the upward movement of the fission-product band during desorption exceeds the mechanical downward movement of the bed as a whole, fission-product activity is carried from the bed to the product receiver. Increased sodium fluoride discharge (25 to 30% per run) and back-purging of fission products are both planned during future runs to prevent this.

Only the Ru^{106} and Sb^{125} decontamination factors were affected by the fission-product carryover. A gradual increase in Tc^{99} activity ($T_{1/2}$, 2.1×10^5 years) in the product occurred after run R-1 (see Table III-2), probably from net upward migration in the absorber. The uranium hexafluoride met AEC specifications for enriched uranium[4] except for molybdenum and for gross β activity (which was high because of Tc^{99}).

Modifications are being made in the pilot plant to improve the quality of the uranium hexafluoride product. Inert-gas inleakage to the sodium fluoride absorber, which became serious in runs R-5 and R-6, will be eliminated by replacing the flanges with welds. Equipment improvements include the installation of a magnesium fluoride pellet bed for the removal of Tc^{99} (and possibly Np^{237}) from uranium hexafluoride. Also, selective desorption techniques will be used to remove molybdenum hexafluoride from the absorber bed prior to bulk uranium hexafluoride desorption. The installation of a constriction-response type uranium hexafluoride analyzer in the absorber off-gas line is expected to aid in the evaluation of the various methods for improving product purity.

Corrosion in the ORNL Volatility Pilot Plant. Following a series of runs with active material, a leak was observed during a scheduled inspection of the hydrofluorinator-dissolver of the Volatility Pilot Plant. The pilot plant had been

Table III-2 CATION IMPURITIES IN URANIUM HEXAFLUORIDE PRODUCT OF VOLATILITY PROCESS[1]

Run No.	Amount, ppm of UF_6 (except Pu, ppb)												
	Cr	Cu	Fe	Li	Mo	Na	Ni	Sn	Zr	Np	Tc	Pu	Total
R-1	130	83	24	<1	32	155	52	<1	<1	157	<1	<1	<637
R-2	12	12	40	<1	350	180	15	<5	<3	177	69	<1	<864
R-3	<80	17	6	<1	130	96	1	<4	<4	8	59	<1	<406
R-4	<1	27	13	<1	560	335	<5	<10	<5	3	159	<1	<1119
R-5	<1	38	14	<1	4300	290	9	<5	<5	188	685	<1	<5536
R-6	62	<8	53	<1	283	54	3	<6	<3	1315	1210	<1	<2998

decontaminated with aqueous solution to background levels of less than 50 mr/hr, and the leak was detected after an exterior salt encrustation at the bottom of the dissolver was found. The crust contained both process salt and aluminum nitrate used in decontamination.[5,6]

It was deduced that the leak probably developed during run R-1, the first in the series of six runs made with irradiated zirconium-uranium alloy fuel. A $1\frac{1}{2}$-ft-high section at the bottom of the dissolver was removed for remote metallography. It was found that the leakage was through two intersecting cracks — one crack, which was horizontal and about $1\frac{1}{8}$ in. long, was located between the lowest girth weld and the attachment welds for two stainless-steel-sheathed thermocouples; the other crack, which was vertical and about $\frac{3}{8}$ in. long, was also located between the thermocouple welds.

Sections of the dissolver were examined metallographically by ORNL Metallurgy and Ceramics Division personnel. The major cracks were thought to have been of external origin and related to metal preparation and to attachment of the two thermocouple beads. Regularly spaced internal horizontal cracks as much as 40 mils deep were found at several locations in the lower section. No such cracks were observed in a ring of metal between the upper girth weld in the section removed and in the cut severing the removed section. This ring of metal was taken as typical of the remaining lower section of the dissolver. Chemical analyses are being made to determine whether the section of the vessel that failed had been made from a heat of INOR-8 known to be substandard.[7]

In order to evaluate corrosion in the fluorinator, two 4-in.-diameter disks were removed and subsequently examined by Battelle Memorial Institute (BMI) personnel. The normal L-nickel intergranular attack was noted in the base metal but was not present in the INCO-61 welds.

In an attempt to account for a certain amount of weld attack observed in the fluorinator, aqueous decontamination conditions used for the fluorinator were simulated insofar as possible in a laboratory study at BMI. The L-nickel specimens corroded in 0.1*M* $Al(NO_3)_3$–0.01*M* HNO_3 (AN-N) at boiling temperature, with rates ranging downward from 250 to 20 mils/month. Solutions of 5-2-2 wt.% sodium hydroxide–sodium tartrate–hydrogen peroxide (CTP) at room temperature gave corrosion rates for L-nickel ranging from 1.6 to 8 mils/month. The INCO-61 weld-rod specimens corroded at rates less than half those of L-nickel, but the INCO-61 weld in L-nickel specimens cut from the Volatility Pilot Plant fluorinator showed a definitely higher rate of attack than did the adjoining L-nickel. Coupons welded with INCO-61 also showed a region of accelerated attack at the junction of the weld and the base metal. Specimens of INOR-8, the metal from which the dissolver is made, were attacked only very slightly by AN-N and CTP solutions. A three-step 68-hr decontamination of the ORNL bench-scale INOR-8 dissolver with AN-N solution at about 90°C resulted in an average corrosion penetration of 3 mils (about 0.3 mil/month). Thus AN-N appears to be a satisfactory decontamination reagent for INOR-8 but is not satisfactory for the L-nickel and INCO-61 welds under the conditions used.

Further analysis of corrosion under processing conditions has been carried out for nickel-base alloy specimens exposed in the Volatility Pilot Plant Mark III fluorinator.[8] Corrosion tests of potential container materials and of the first two fluorinators were reported earlier.[9–11] All three fluorinators have sustained a maximum corrosion attack of approximately 1 mil/hr, based on fluorine exposure times.

In the present tests, one set of specimens was exposed[12] during Volatility Pilot Plant runs T-1 through T-7 and another in runs TU-1 through TU-5. In the former series no uranium was contained in the salt, whereas in the latter 0.3 wt.% uranium was contained. The LiF-NaF-ZrF_4 salt composition was approximately 30-27-43 mole %. Temperatures ranged from 500 to 510°C during the fluorination. Fluorination times were 12 and 10 hr in the two series of tests, and total salt exposure times were 367 and 205 hr. Nickel and a variety of nickel alloys containing minor amounts of iron, manganese, cobalt, and aluminum were tested.

Dimensional changes were measured and metallographic examination was made on all samples. Metallographic examination revealed that corrosion had caused one or more of the following: (1) surface films, (2) surface attack, (3) intergranular attack, and (4) grain-boundary modification.

Several conclusions can be drawn from the results reported in the fluorination-corrosion tests. These conclusions are in agreement with those obtained in the previous test series:

1. The combination of an operating temperature near 550°C and the presence of lithium

fluoride in the salt baths produces about the same bulk metal losses on nickel and nickel-base alloys as were found by operating at 650°C with lithium absent.

2. The presence of uranium accelerates the corrosion of nickel and nickel-base alloys during the volatility-process fluorination cycle.

3. Prior fluorine conditioning of L-nickel decreases the rate of corrosion of the material during subsequent fluorination.

4. Prior fluorine conditioning of INCO-61 weld metal increases the attack on INCO-61 during subsequent fluorination.

5. When fluorination is performed at 550°C with lithium present in the fluoride salt bath, bulk metal losses of L-nickel are about the same as those of the nickel binary alloys containing manganese, iron, cobalt, or aluminum.

6. The presence of the alloying elements, manganese, iron, or aluminum, in nickel drastically reduces or eliminates the intergranular attack usually found in unalloyed nickel exposed to a fluorination environment.

7. In fluorination environments the effect of adding cobalt to nickel on subsequent corrosion by intergranular attack of the binary is unclear. These reported tests showed that serious intergranular attack of a 95 nickel–5 cobalt specimen occurred. On the other hand, this test series and previous series showed good resistance to this form of corrosion by nickel containing 10 and 20 wt.% cobalt.

8. Unalloyed nickel of greater than commercial purity shows less resistance to bulk metal losses, integranular attack, and grain-boundary modifications when exposed to fluorination environments than does L-nickel and all nickel alloys tested.

Basic Corrosion Studies in Fused Salt. A summary report has been issued on the corrosion properties of alloys based on the nickel-molybdenum system in fused-salt media. An analytical approach for the prediction of corrosion rates in these media is presented which is based on thermodynamic properties of the alloy and fluoride salt mixture. Although the effects of sparging with fluorine or hydrogen fluoride are not treated, this paper presents (1) results of corrosion experiments dealing with fluoride salts tested in support of the Molten-Salt Reactor Experiment at ORNL and (2) analytical methods employed to interpret corrosion and mass-transfer behavior in this reactor system.[13] Another report discusses the development of radiotracer techniques for use in these studies of corrosion by molten fluorides.[14]

Corrosion Tests of Alloys in Fused Salt. At BMI, nickel-iron-molybdenum alloys continue to be evaluated for use in the hydrofluorinator-dissolver of the ORNL pilot plant. Test specimens included[15] INOR-8 and Alloy 79-4, which had previously shown the most promising results, along with about 10 other alloys of slightly different compositions. The overall range of alloy compositions was nickel (71 to 85%), iron (5 to 20%), and molybdenum (2 to 16%). Samples were exposed to hydrogen fluoride at 650°C under the following two salt compositions:[5,16] (1) NaF-LiF-BeF_2 (50.5-37.0-12.5 mole %) and (2) NaF-LiF-ZrF_4 (37.5-37.5-25 mole %). In these tests, INOR-8 showed the least attack. The composition of INOR-8 (in wt.%) is 71 nickel, 5 iron, 16 molybdenum, and 7 chromium.

The NaF-SbF_5 Complex

Interest in the sorption of antimony pentafluoride (SbF_5) on sodium fluoride has followed the observation that there was Sb^{125} contamination of uranium hexafluoride in some runs with active material in the ORNL Volatility Pilot Plant.[16] In preliminary experiments, NaF/SbF_5 mole ratios of about 4 were observed for 12- to 20-mesh sodium fluoride. The dissociation pressure of the complex was measured at less than 0.4 mm Hg in the range of 210 to 305°C.

Plutonium Volatilization from Fused Salt

The volatilization of PuF_6 from fused salt by direct fluorination was about the same at an initial plutonium concentration[6] of 960 ppm as in previous[17] work where only 2 ppm was used.[18] The data in both experiments appear to follow a first-order concentration rule, with a half-value period of about 3 hr. In the present test a total of 89.3% of the plutonium was volatilized in 10 hr using LiF-NaF-ZrF_4 (31-24-45 mole %) at 600°C. The overall material balance was 97.8%, with 84.8% being trapped on consecutive CaF_2 and NaF beds at 100°C. Of the plutonium charged, a small amount, 0.5%, was retained on the wall of the nickel fluorinator vessel.

Preparation and Properties of Volatile Fluorides

Separation of Technetium from Uranium Hexafluoride. In the processing of uranium fuels

from nuclear reactors, uranium is purified from associated fission products by solvent-extraction techniques. The purified uranium product from the solvent-extraction process is converted to uranium trioxide and then fluorinated to uranium hexafluoride for feed to the gaseous diffusion cascades for U^{235} enrichment. Due to the solvent-extraction characteristics of technetium, some of this element accompanies the uranium during the purification process and is found as a contaminant in the uranium hexafluoride product.

A method for recovering technetium from a uranium hexafluoride gas stream, which is based on selective sorption on inorganic fluorides, has been developed at the Union Carbide Nuclear Company.[19] Several inorganic fluorides were evaluated as sorption agents on the basis of quantity of technetium sorbed. Of the fluorides tested, magnesium fluoride appeared most suitable since it exhibited a high capacity for technetium, it is practically insoluble in water, it is available as a high-surface-area powder, its uranium sorption is low, and it is relatively inexpensive. Laboratory tests performed with beds of $\frac{1}{4}$- to $\frac{1}{8}$-in.-diameter pellets of magnesium fluoride showed that the sorption efficiency of magnesium fluoride for technetium is dependent on the gas velocity or gas retention time in the pellet bed. At a superficial gas velocity of 0.95 ft/sec, the recovery efficiency was a maximum of 83% at the beginning of the test and decreased rapidly to 40%. At a velocity of 0.27 ft/sec, the recovery efficiency was greater than 99% until 2.8 g of technetium had been fed to the bed. This weight of technetium corresponds to 0.77 wt.% technetium in the pellet bed.

A sorption recovery system has been installed and operated at the Paducah plant of the Union Carbide Nuclear Company. The system consists of two sorption units in parallel, each unit 40 in. in diameter and 48 in. high. The units each contain 1100 lb of magnesium fluoride pellets sized between $\frac{1}{4}$ and $\frac{1}{8}$ in. The traps are located in the uranium hexafluoride stream immediately after the oxide fluorination towers. During normal operation the pressure drop across the sorption columns was less than 0.5 psi. The temperature of the gas stream at the sorption units was near 94°C. In the first plant-scale test, uranium hexafluoride containing trace quantities of technetium was processed through the columns, and approximately 96% of the technetium was retained on the magnesium fluoride pellets. The technetium was leached from the magnesium fluoride by circulating 285 gal of water at room temperature through each unit. Approximately 4.6 kg of technetium, equivalent to 93% of that retained on the magnesium fluoride pellets, was recovered by leaching. The solution contained 2.1 g of technetium per liter, 4 g of fluorine per liter, 3 g of uranium per liter, and other metallic impurities. The technetium was subsequently purified and recovered by ion exchange.

Preparation of Transition-Metal Fluorides and Oxytetrafluorides. Edwards, Peacock, and Small[20] have described methods for the preparation of molybdenum pentafluoride and have determined the structural unit of the solid phase. The compound was conveniently prepared by the reduction of molybdenum hexafluoride by molybdenum carbonyl or tungsten carbonyl at 25°C and by the reduction of the hexafluoride with molybdenum metal powder at 300 to 400°C. The preparation of molybdenum pentafluoride by reaction of dilute fluorine with molybdenum powder at 400°C results in an impure product that is contaminated with a large proportion of molybdenum oxytetrafluoride.

Pure molybdenum pentafluoride is a yellow, crystalline solid that melts at 67°C to a viscous yellow liquid. As the temperature is raised, the liquid becomes more mobile, but at 150°C the compound begins to disproportionate irreversibly to the hexafluoride and a solid phase that is believed to be molybdenum tetrafluoride. The structural unit of the solid pentafluoride was determined by X-ray techniques to be a tetramer with the molybdenum atoms at the corners of a square. The metal atoms are linearly linked by bridging fluorine atoms.

Ruthenium metal readily reacts with fluorine at temperatures between 280 and 900°C to give a dark-green viscous liquid. Holloway and Peacock[21] have recovered ruthenium pentafluoride from this mixture by distilling the liquid under vacuum. A nonvolatile solid containing ruthenium metal and ruthenium dioxide remains behind. Ruthenium pentafluoride is a dark-green crystalline solid that melts at 86.5°C. The boiling point was found by direct measurement to be 230°C. The vapor pressure for liquid ruthenium pentafluoride in the temperature range 90 to 160°C may be represented by $\log P_{mm\ Hg} = 9.54 - 3329/T$. The calculated heat of vaporization is 15,230 cal/mole.

Holloway and Peacock[21] have also measured several physical constants of ruthenium oxytetrafluoride ($RuOF_4$). The compound was prepared by the action of bromine trifluoride and bromine on ruthenium metal at 20°C. Ruthenium oxytetrafluoride forms colorless crystals that melt at 115°C. The vapor-pressure equation for the solid (20 to 110°C) is $\log P_{mm\ Hg} = 9.22 - 2857/T$, and for the liquid (120 to 160°C) is $\log P_{mm\ Hg} = 8.60 - 2616/T$. The boiling point, found by extrapolation of the vapor-pressure data, is 184°C. The heat of vaporization of ruthenium oxytetrafluoride was calculated to be 11,970 cal/mole.

Chemical Reactions Involving Hexafluorides. The reactions of molybdenum hexafluoride, tungsten hexafluoride, and uranium hexafluoride with liquid and gaseous dinitrogen tetroxide have been studied by Geichman and associates at Goodyear Atomic Corporation.[22] Uranium hexafluoride reacts with both liquid and gaseous dinitrogen tetroxide to give the complex salt, nitrosylium hexafluorouranate(V), $NOUF_6$. This compound has been previously reported by Geichman et al.[23] as the product of the reaction of uranium hexafluoride with nitric oxide. When molybdenum hexafluoride is mixed with liquid dinitrogen tetroxide at 25°C, a white solid having the empirical composition $NOMoOF_5$ is obtained.[22] The overall reaction for the formation of nitrosylium pentafluoroxymolybdate(VI) can be represented as

$$2MoF_6 + 3N_2O_4 \xrightarrow[N_2O_4]{\text{liquid}} 2NOMoOF_5 + NO_2F + NOF + N_2O_5$$

In the gas-phase reaction between MoF_6 and N_2O_4, the compound $NOMoOF_5$ is produced; however, no evidence was found for N_2O_5 or NOF among the reaction products. It was observed that the reaction between tungsten hexafluoride and liquid and gaseous dinitrogen tetroxide produced a solid compound $NOWOF_5$, which is analogous to that produced in reactions with molybdenum hexafluoride.

Gaseous uranium hexafluoride and nitrogen dioxide react[24] instantaneously at 25 and 60°C under conditions of low partial pressures of nitrogen dioxide to form solid nitrylium hexafluorouranate(V), NO_2UF_6. The presence of nitryl fluoride as a reaction product suggests that the reaction between uranium hexafluoride and nitrogen dioxide proceeds by the formation of uranium pentafluoride and nitryl fluoride which then combine to form NO_2UF_6. This method for preparing NO_2UF_6 was demonstrated in a test in which excess gaseous nitryl fluoride was mixed with UF_5 at 25°C. The product of this reaction was NO_2UF_6, which gave an infrared spectrum identical to that obtained from the product of the reaction between nitrogen dioxide and uranium hexafluoride. Neither molybdenum hexafluoride nor tungsten hexafluoride appears to react with nitrogen dioxide.

Nitrylium hexafluorouranate(V), is a yellowish-white solid having no detectable vapor pressure at 25°C. It is soluble in anhydrous hydrogen fluoride but insoluble in carbon tetrachloride. The solid density was observed to be 3.9 g/cm^3. The solid undergoes relatively slow hydrolysis in air and rapid hydrolysis with excess water according to the equation $2NO_2UF_6 + 4H_2O \rightarrow UF_4 + UO_2F_2 + 2HNO_3 + 6HF$.

O'Donnell and Stewart[25] have reported the results of a detailed study on the chemical reactions of molybdenum hexafluoride with the fluorides of certain elements of Periodic Groups V and VI and with Group V trichlorides.

Fluoride Complexes of Pentavalent Uranium. Fluoride complexes of pentavalent uranium have been prepared by Penneman, Asprey, and Sturgeon[26] by the direct combination of uranium pentafluoride with ammonium fluoride at 80 to 85°C or with alkali fluorides in a sealed bomb at 350 to 400°C. The product of heating NH_4F with UF_5 (1:1 mole ratio) at 85°C has a characteristic X-ray powder pattern different from those of the starting materials. On treatment with water the compound $UF_5 \cdot NH_4F$ disproportionates instantly, giving a solution containing yellow uranyl ion and a green solid identified as $UF_4 \cdot NH_4F$. If 48% HF is used to dissolve $UF_5 \cdot NH_4F$, a stable solution of U(V) is obtained. On addition of a saturated solution of rubidium fluoride to hydrogen fluoride solutions of U(V), the compound $UF_5 \cdot RbF$ is precipitated as ice-blue crystals.

A pale blue powder is obtained by grinding together anhydrous rubidium fluoride with uranium pentafluoride in a 1:1 mole ratio and heating for 16 hr in a nickel bomb at 400°C. The product gives an X-ray powder pattern identical with that of $UF_5 \cdot RbF$ obtained from hydrogen fluoride solutions.

Pyrometallurgical Processes

Pyrometallurgical processes for recovery of discharged reactor fuel materials include processes in which metallic fuels are processed directly as metals and those processes in which both metallic and ceramic fuels are processed in liquid-metal–salt solvent systems. The potential economic advantages of these processes lie in their ability to process short-cooled fuels, which permits a reduction of fuel inventories, and in the avoidance or simplification of chemical conversions.

Melt Refining

The Fuel-Cycle Facility that has been built adjacent to the Experimental Breeder Reactor No. 2 (EBR-II) at the National Reactor Testing Station (NRTS) in Idaho will serve not only to recover discharged EBR-II fuel material but also as a pilot plant for demonstrating various pyrometallurgical processes. Progress continues to be made toward making this facility ready for processing EBR-II fuel.[27] It is expected that the first fuel will be discharged from the reactor in mid-1964. The facility consists principally of two cells, an air-atmosphere cell (Air Cell) where those operations which do not expose the fuel to the atmosphere are conducted and an argon-atmosphere cell (Argon Cell) in which exposed fuel may be safely handled and processed. Melt refining, the process to be employed for purification of the first discharged EBR-II fuel, will be performed in the Argon Cell. Melt refining is a simple melting process in which fission products are removed from molten uranium at 1400°C by vaporization and by selective oxidation reactions.

A negative cell pressure of 2 in. of water will be employed in normal operation of the 66,000-cu ft Argon Cell. The maintenance of a low-oxygen (less than 100 ppm) argon atmosphere in the cell will require that the inleakage rate of air be very low (less than 0.01 cfm). Recent measurements of the air inleakage rate into the Argon Cell disclosed a satisfactorily low inleakage rate of 0.006 cfm at a cell pressure[27] of −4 in. H_2O. With the cell purification system in operation, oxygen concentrations in the nitrogen (which was employed as a substitute for argon in these preliminary tests) ranged between 8 and 30 ppm; the water concentration[27] was about 5 ppm. These low levels of oxygen and water contamination are considered to be very satisfactory.

Although the Argon Cell of the EBR-II Fuel-Cycle Facility now includes equipment for the removal of oxygen and water from the argon atmosphere of the cell, no special provisions have been made for the removal of nitrogen from the Argon Cell gas. The nitrogen concentration in the argon will reach an equilibrium level that will be dependent on the rate of air inleakage and on the rate at which the Argon Cell gas is purged with pure argon. The equilibrium nitrogen concentration will probably be well under 5%. Because the presence of nitrogen in the cell atmosphere might cause problems in processing fuel materials, depending on the nature of the fuel material being processed, removal of nitrogen from the Argon Cell atmosphere may ultimately be required. This has prompted a study by Argonne National Laboratory (ANL) of the removal of nitrogen from argon by gettering the nitrogen with titanium sponge.[27] The study is being carried out in two parts: (1) the study of the kinetics of the titanium-nitrogen reaction and (2) construction and operation of a scale model of the proposed plant system. Preliminary data have indicated that the reaction rate is controlled by diffusion of nitrogen in the solid.

A procedure has been developed for the removal of sodium from a discharged EBR-II fuel subassembly while the subassembly is in the coffin that will be used for transporting a subassembly between the EBR-II reactor building and the Fuel-Cycle Facility.[27] Sodium will first be slowly converted to the oxide by circulating argon containing a small quantity of air through the subassembly. The oxide will then be converted to the hydroxide by humidifying the added air, after which the hydroxide will be flushed away with water.

While a subassembly is being transported in the coffin, it will normally be cooled by circulating argon through it. An emergency cooling system has been developed which consists of flooding the coffin with mercury for conduction of heat from the subassembly to the coffin body.[27] In the event of its use, the heat of reaction between the mercury and the sodium present on the subassembly would result in a temperature rise of less than 100°F in the mercury.

Development of Liquid-Metal and Salt Processes

Molten metals and salts are employed as solvent media for reactor fuel materials in processes that are under development at several atomic energy sites. Purification of reactor fuel materials in liquid metals and salt systems is effected by selective extraction of product or impurity elements, by selective precipitation of elements using favorable solubility or concentration relations, and by vaporization of volatile species.

The skull reclamation process, which is being developed at ANL, complements the melt-refining process in the EBR-II fuel cycle and serves to reclaim and purify fissionable material contained in crucible residues or skulls from the melt-refining process. The flow sheet for the skull reclamation process was given in the October 1962 issue of this Review.[28] The process consists essentially of selective extraction of noble-metal fission products into zinc (which is discarded) from a uranium oxide–fission-product–molten-salt slurry, a subsequent extraction of uranium into a magnesium-zinc solution, two selective precipitations of uranium from metal solutions to effect further uranium purification, and a final retorting step to isolate the uranium metal product.

Construction of a pilot plant for relatively large-scale demonstrations of the skull reclamation process has been completed.[27] The major processing vessels are two large, normally stationary crucibles that are positioned centrally within metal bell jars. One of these crucibles, a 500-lb pressed-and-sintered tungsten crucible (12 in. in outside diameter by 19 in. high) serves for the first two steps of the process; the other, a beryllia crucible of about the same size, serves for the two precipitation steps. The uranium concentrate (uranium enveloped in a 50% magnesium-zinc alloy) will be removed and retorted in another beryllia crucible.

The metal bell jars are about 30 in. in diameter and 40 in. high and can be tightly closed for containment of a high-purity argon atmosphere. Heating will be effected by means of graphite susceptors heated by radiant-cooled copper induction coils. Solution removal for the necessary phase separations will be effected by pressuring the liquid out through dip tubes (pressure-siphoning).

The integrated equipment with the bell-jar covers in place is shown in Fig. III-1. A transfer line is shown in position for transfer of molten metal from one furnace to the other. In Fig. III-2 the bell-jar cover has been removed from one furnace, showing the large pressed-and-sintered tungsten crucible (12 in. in outside diameter by 20 in. high, weighing 500 lb) in position within the induction heating coil. A somewhat similar large beryllia crucible will be contained in the other furnace. Ultimately this equipment will be enclosed in a glove box, the frame of which is shown in Fig. III-1, allowing operation in an inert-argon atmosphere. Preliminary operation has been started in air in order to determine any necessary equipment corrections or changes in operating procedures.

Distribution of Elements Between Immiscible Phases

Distribution coefficients of various elements between molten metal and molten-salt phases are being determined at ANL to assess the possibility of separating uranium and plutonium from rare earths and yttrium by fused-salt extraction. In equilibrated systems of magnesium-zinc alloys and molten magnesium chloride at 800°C, uranium, plutonium, and thorium distribute preferentially into the salt phase. The distribution coefficients (concentration in flux/concentration in metal) of the rare earths differ from those of uranium, plutonium, and thorium[29,30] by a factor of about 40, so that appreciable separation of these two groups of elements can be achieved in a few stages of countercurrent extraction. Recently, distribution data have been obtained for neptunium and curium.[27] The distribution coefficients of these elements are similar to those of plutonium, uranium, and thorium. Since americium distributes preferentially into the salt phase, a molten-salt–metal extraction procedure could be used to effect a separation of americium from curium and plutonium. All the available distribution data[27,29–31] are plotted in Fig. III-3.

In connection with the development of a process for removal of fission products from the uranium-bismuth fuel solution of the Liquid-Metal Fuel Reactor (LMFR), the distributions of uranium and a rare earth, cerium, were measured at 500°C between dilute solutions of magnesium in bismuth and a eutectic NaCl-KCl-$MgCl_2$ on a kilogram scale in metallic containers.[32] The cerium distribution coefficient

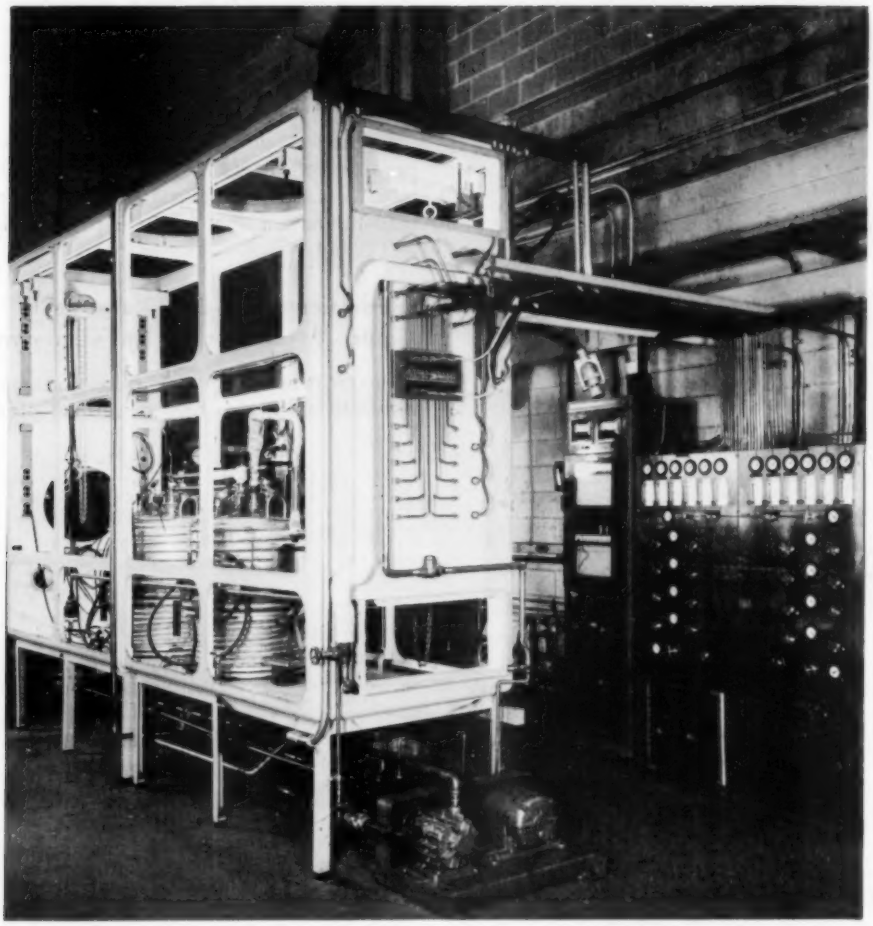

Fig. III-1 Skull reclamation pilot plant.[27] The glove box (at left), which contains two bell-jar processing furnaces, will not be furnished with windows during preliminary work. The panelboard is at the right.

(concentration in salt/concentration in metal) was a reproducible function of the magnesium concentration in the bismuth phase, decreasing with increasing magnesium concentration (Fig. III-4). A similar but somewhat less reproducible relation was found for uranium (Fig. III-5), but the values of its distribution coefficient were considerably lower than that for cerium. The values of the separation factor (ratio of cerium distribution coefficient to uranium distribution coefficient) are about 420. The distribution coefficients were not affected by phase weight ratios or by the use of two different container materials, 347 stainless steel or molybdenum.

Separation of Plutonium from EBR-II Blanket Material

For the EBR-II cycle, a process for separating plutonium from blanket material has been developed at ANL.[28] This process is currently undergoing scale-up. An alternative blanket process has been investigated briefly at Argonne. In this process, uranium and plutonium were first oxidized into a molten halide flux by zinc chloride at 800°C and subsequently reduced at 800°C from the flux phase with magnesium metal. The reduced plutonium dissolved in excess magnesium reductant, whereas uranium, which has a very low solubility in

Fig. III-2 Furnace (with bell-jar cover removed) for noble-metal extraction and oxide reduction.[27] Shown inside the furnace wall are the induction coil, the Fiberfrax insulator, the graphite susceptor, and a new 12-in.-OD tungsten crucible, inside of which part of an integral baffle may be seen. In the background is the induction heating station.

magnesium, precipitated. All reactions behaved as expected, but separation of precipitated uranium from the magnesium supernatant solution was poor. Work is under way to improve this separation.

Separation of Uranium from Fission-Product Elements

Park of the National Bureau of Standards has attempted to employ the formation of either a uranium compound or compounds containing fission-product elements as a method of separating uranium from fission products.[33] Separation of uranium from molybdenum or ruthenium by zone melting after additions of various third elements was unsatisfactory. Mechanical separation by screening powdered uranium–impurity-element compounds that had been produced by hydriding-dehydriding uranium alloys was also attempted. This technique was judged impractical because of the difficulty of handling finely divided uranium. Selective reactions in mercury and zinc systems were investigated qualitatively; some of these were reported to have promise as methods of separating uranium from fission products.

Pumpable Dispersions of Intermetallic Compounds in Liquid Metals

A method of preparation of pumpable dispersions of thorium-bismuth and thorium-lead intermetallic compounds in lead, bismuth, or lead-bismuth alloys has been patented by Teitel and Cobel.[34]

Fundamental Studies Relative to Liquid-Metal Process Development

Solubilities of fission-product elements, fissionable elements, and structural elements in

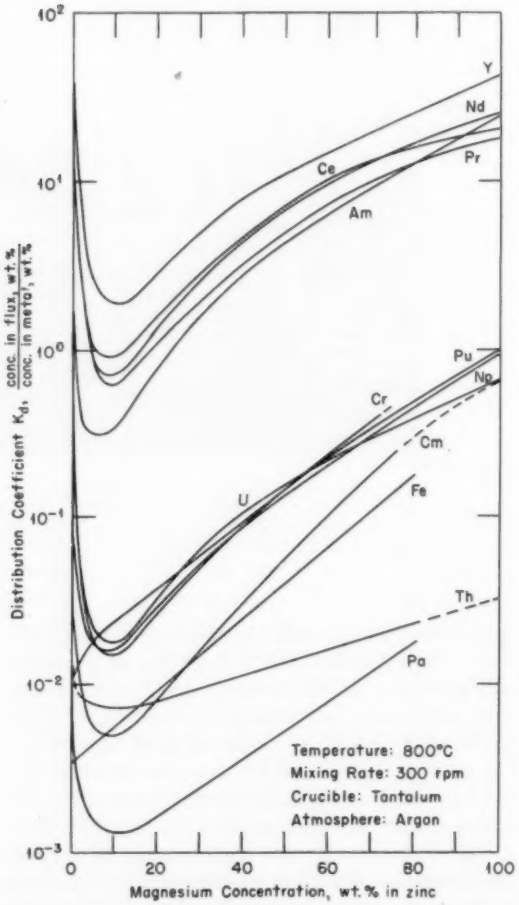

Fig. III-3 Distribution of selected elements between zinc-magnesium alloy and magnesium chloride. (Based on data in Refs. 27 and 29 to 31.)

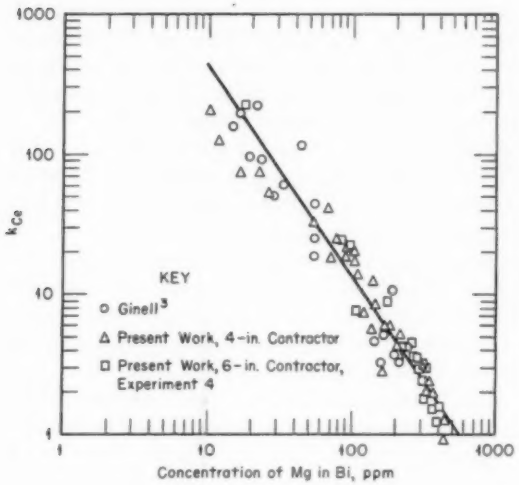

Fig. III-4 Distribution of cerium between bismuth-magnesium and NaCl-KCl-$MgCl_2$ eutectic[32] at 500°C. Note: "Ginell[3]" in the key is W. S. Ginell, *Ind. Eng. Chem.*, 51: 185 (1959).

liquid-metal solvents are necessary information for the development of liquid-metal processes. The solubilities at various temperatures of barium and neodymium in liquid zinc have recently been reported.[27] The solubility of barium decreases rapidly from 0.45 wt.% at 710°C to 0.005 wt.% at 560°C and may, over this temperature range, be represented by the equation: log (wt.% barium) = 10.464 – 10,640 T^{-1}. The solubility of neodymium ranged from 2.0% at 750°C to 0.005% at 450°C. A peritectic transformation is evident at about 700°C.

Mulford of Los Alamos has recently tabulated thermodynamic functions for pure plutonium over the temperature range[35] of 298.16 to 2500°K. At Argonne the thermodynamic quantities for plutonium-zinc systems are being determined by electromotive-force measurements in a galvanic cell. The free energy of formation of Pu_2Zn_{17} and the activity of plutonium in saturated zinc solutions have been reported.[27] Compounds in the yttrium-zinc system have been identified by effusion and X-ray studies.[27]

In a discussion of the solubilities of rare earths in cadmium on page 31 of the preceding issue of this Review, it was reported that the equilibrium solid phases were MCd_6 for light rare-earth elements up to samarium and MCd_{11} for heavy rare-earth elements. This statement is in error and should be corrected so as to state that MCd_{11} is the equilibrium phase for the light rare-earth elements up to samarium and MCd_6 is the equilibrium phase for the heavy rare-earth elements.

Construction Materials

The Los Alamos Molten-Plutonium Reactor Experiment (LAMPRE-I) is a 1-Mw materials testing reactor for the evaluation of molten-plutonium alloy fuels and their container materials. A series of three papers has been published on the following subjects: (1) the development of high-purity tantalum and its alloys for the containment of LAMPRE-I fuels,[36] (2) the corrosion testing and fuel alloy selection for LAMPRE-I,[37] and (3) the fabrication of tantalum fuel containers.[38] The plutonium–10 at.% iron fuel alloy of the first LAMPRE loading was sealed in capulses 8 in. long and 0.430 in. in diameter[36] which were fabricated from an ultrapure tantalum–0.1% tungsten alloy. Corrosion resistance of tantalum was improved by additions of either tungsten (up to 10 wt.%) or yttrium (to 0.2 wt.%), although during arc melting of tantalum (to consolidate and purify it) the yttrium was distilled out. Zirconium, hafnium, thorium, and carbon were

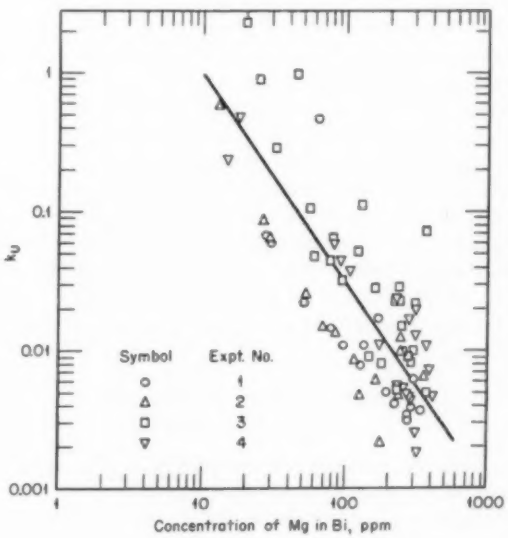

Fig. III-5 Distribution of uranium between bismuth-magnesium and NaCl-KCl-$MgCl_2$ eutectic at 500°C, showing data from all experiments.[32]

distinctly harmful alloying additions to the containment material. Of the interstitial alloying elements, hydrogen, nitrogen, and carbon in small amounts had no effect on corrosion; oxygen was found to promote plutonium attack on the container metal.[36]

Corrosion of the tantalum–0.1% tungsten alloy was strongly influenced by fuel alloy composition.[37] All levels of calcium and magnesium in the fuel were detrimental. The addition of carbon (200 to 400 ppm), silicon (0.4 to 1.5 wt.%), or aluminum (0.3 to 0.7 wt.%) reduced intergranular attack of the tantalum at temperatures[37] up to 750°C. The carbon also essentially eliminated mass transfer of the tantalum.[37]

An impact extrusion and ironing procedure was employed to fabricate the tantalum capsules. Details of this procedure have been discussed by Hanks, Kirby, and Taub.[38]

On Sept. 15, 1962, after 988 Mw-hr of operation of LAMPRE-I, leakage of fuel from a capsule (all of which were upright) occurred.[39] The capsule was removed, and on the basis of extensive examination, it was tentatively concluded[39] that the failure was initiated by severe localized intergranular penetration through the top weld. Fuel foamed, leaked out of the weld, and ran down the side of the capsule. By dissolution of the capsule wall below the liquid level, it created a hole in the capsule, permitting additional leakage of the fuel. Because intergranular penetration of this and adjacent capsules was observed only in the weld zone, and because such intergranular attack had previously been observed in tantalum that contained appreciable oxygen, it is suspected that oxygen contamination occurred during closure welding. Efforts are being initiated to improve welding procedures and to reexamine the effect of the oxygen content of tantalum on corrosion by the molten-plutonium-iron alloy. Also continuing is the study of the corrosion of tantalum alloys by plutonium-cobalt and plutonium-cobalt-cerium alloys.[39,40]

Container Materials for Molten Uranium and Uranium-Base Alloys

Suitable container materials are also being sought for molten-uranium-base alloys.[39,40] The containment of uranium-manganese-plutonium alloys has been given principal attention. Crucibles of TaC, NbC, and ZrC suffered intergranular attacks of 1.5, 10, and 13 mils, respectively, in holding a 78 at.% uranium–22 at.% manganese alloy at 1100°C for 210 hr.[39] Yttrium also shows promise as a container material. In 500 hr at 900°C, yttrium capsules suffered a penetration of 2.5 mils on exposure to the above uranium-manganese alloy and a penetration of less than 1 mil on exposure to a 73 at.% uranium–5 at.% plutonium–22 at.% manganese alloy.[40] The presence of plutonium appears to reduce the attack on yttrium.

The penetration rates of stainless steel by molten uranium and uranium-fissium alloys at temperatures of 1100 to 1350°C have been measured by Walter and Kelman of ANL.[41] This information, which indicates the rate of escape of molten uranium through stainless-steel claddings during a reactor excursion, has particular relevance to the EBR-II reactor. Penetration rate increased rapidly with temperatures between 1100 and 1150°C. Thereafter it decreased, a phenomenon that was attributed to the temporary formation of an intermetallic compound. At the temperatures studied, penetration rates ranged from 4 to 15 mils/sec for uranium and from 0.6 to 12 mils/sec for a uranium–5% fissium alloy.

Equipment

Because of the possibility of using plutonium as a molten reactor fuel, it was considered desirable at Los Alamos to build and operate subcritical mockups of fuel transfer and pumping systems.[42] The Molten-Plutonium Pump Experiment was a subcritical mockup of a reactor core in which a plutonium-iron alloy was circulated by means of a sodium lift pump.[42] Sodium for lift pumping was circulated by an electromagnetic pump in an isothermal loop at 500°C. The purpose of the test was to study pump characteristics, instrumentation, sodium-fuel separation, and fuel transfer systems.

The operation of the lift pump is illustrated in Fig. III-6. The diameter of the separation pot is 3 in. Lift pumping of the sodium was concluded to be feasible, although absolute flow rates were not determined. The operation of other system components was also evaluated. These components included the fuel transfer system; the electromagnetic pumps for circulating sodium; and instrumentation for pressure, liquid-level, and sodium-flow-rate determinations.

Westerheide, Clifford, and Burnet briefly reviewed centrifugal and electromagnetic pumps

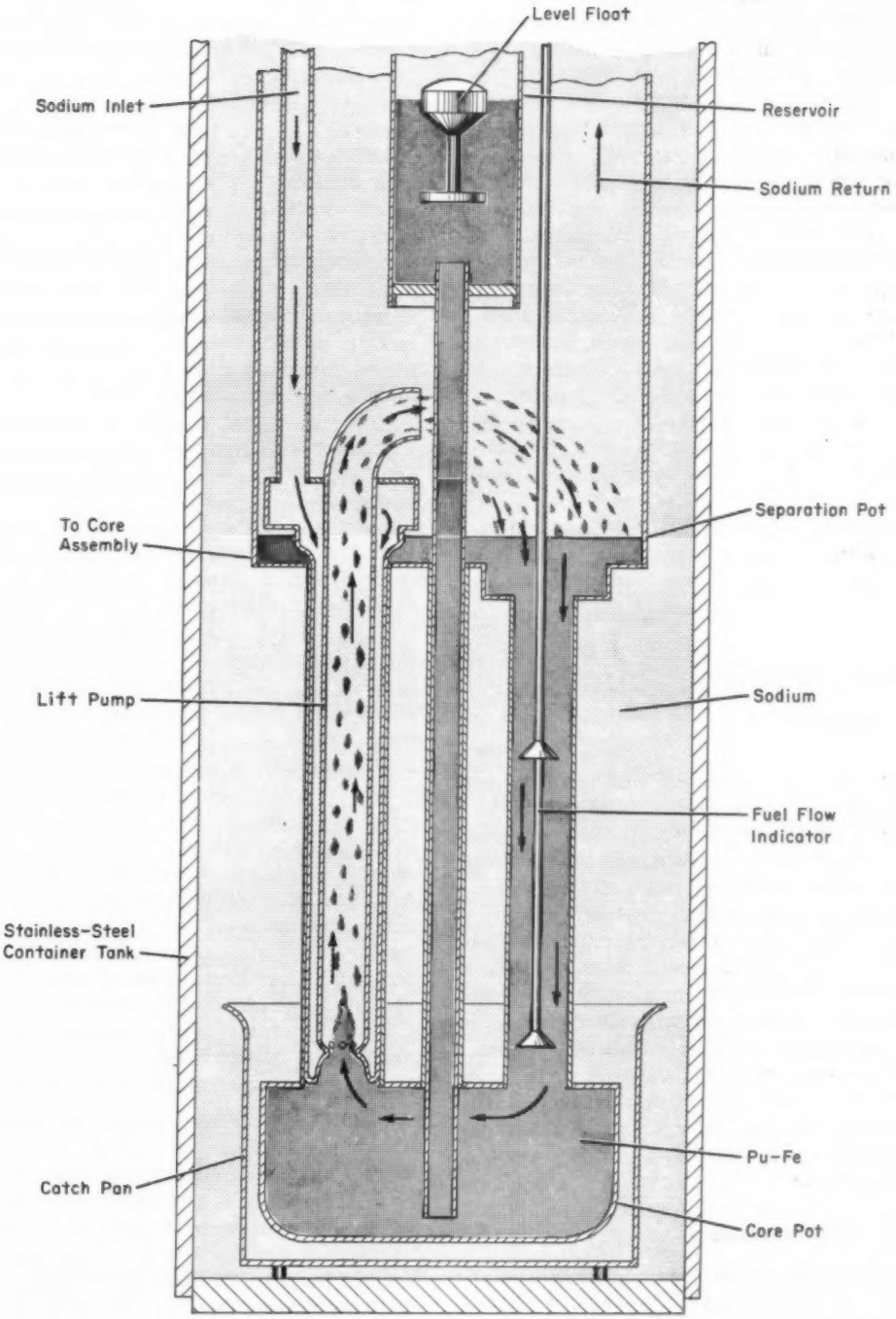

Fig. III-6 Lift pump operation.[42]

for pumping of liquid metals. They then discussed the construction and operation of the first two-stage diaphragm pump to be used successfully in liquid-metal service.[43] This pump was constructed of types 430 and 446 stainless steels and was tested by pumping lead-bismuth eutectic at temperatures between 370 and 575°C. From the results of a 5376-hr test that was arbitrarily terminated, it was concluded that such a pump is well suited to the pumping of liquid metals at low flow rates where pulsating flow can be tolerated. Operating temperature and pressure are limited only by the availability of suitable construction materials.

Armstrong has discussed the mode of operation of electromagnetic pumps in general and the characteristics of various alternative designs.[44] He concluded that electromagnetic pumping is a reliable means of moving liquid metals.

Zone melting above 2000°C has been achieved by Johnson of Ames Laboratory by using an eddy current concentrator with conventional 450-kc induction heating equipment.[45]

Other Nonaqueous Processes

Pyrochemical procedures, which are suitable principally for the processing of oxide and carbide reactor fuels, generally utilize gases, molten salts, and liquid metals as reagents and process media. Characteristics shared by pyrochemical and pyrometallurgical processes are the use of high-temperature reactions, a capability for handling short-cooled fuels, simplicity, and compactness. They differ in that the fuel constituents remain primarily in the metallic state throughout a pyrometallurgical process. By solvent-extraction standards, both types of processes provide low fission-product decontamination, and the fuel cycles for which they are usually considered are closed, remotely operated cycles.

Oxide Fuel Processing

Development work has continued at Hanford[46–48] on the salt-cycle process, a closed-cycle pyrochemical process proposed for the Plutonium Recycle Test Reactor (PRTR). The irradiated uranium dioxide–plutonium dioxide fuel is dissolved in a molten-chloride bath by sparging the mixture with chlorine or hydrogen chloride. A portion of the resulting U(VI) species in solution is reduced electrolytically to plutonium-free uranium dioxide, which is recovered from a graphite cathode as a by-product. The plutonium and uranium remaining in solution are then codeposited electrolytically as a mixture of the dioxides. This product is thereby sufficiently enriched in plutonium so that it can be returned to the reactor after suitable fabrication steps. A first demonstration has been made of the integrated salt-cycle process, in which irradiated uranium dioxide was processed and the product remotely fabricated into a new fuel element.[49] This fuel element was irradiated further without incident. Other chemical and engineering developments on the salt-cycle process during the past year are summarized briefly in a series of quarterly progress reports.[50–53]

The various steps of the salt-cycle process also are being carried out in an engineering demonstration, using one-quarter of an unirradiated fuel subassembly (25 lb of uranium dioxide) per batch.[46] Vibratory decladding equipment for removing uranium dioxide from Zircaloy-clad PRTR fuel-rod segments has resulted in essentially complete recovery (< 0.05% loss) of the uranium from vibratory compacted rods, cold-swaged rods, and hot-swaged rods. Equipment for oxidation of the fuel to U_3O_8 has also been built and tested. Several dissolution-electrolysis experiments have been conducted in a 20-liter silica crucible. The U_3O_8 was dissolved by chlorine sparging at 600°C; both equimolar LiCl-KCl and 2.5 (mole ratio) LiCl-KCl[48] were used as the salt bath.* Then electrolysis with graphite electrodes was conducted at 530°C for 24 hr at a reference potential of 0.7 volt. Reactor-grade uranium dioxide was produced in 25-lb batches.

Thermodynamic values for the reaction

$$UO_2(s) + Cl_2(g) = UO_2Cl_2(\text{solution})$$

were previously reported in Vol. 5, No. 4, page 46, and in Vol. 6, No. 1, pages 36 and 37, of this Review. Some of these values have been revised. A summary of the latest values, calculated for a 1.0 molal UO_2Cl_2 solution, is given in the following table.

*For a more detailed discussion of the electrolytic production of oxide fuel materials from molten-salt media, see Sec. V of this issue.

Melt composition	Temp., °C	ΔG, kcal/mole	ΔS, entropy units	ΔH, kcal/mole
0.42 KCl–0.58 LiCl	550	−25.1	−14.2	−36.8
0.50 KCl–0.50 LiCl	550	−26.2	−15.3	−38.8
0.26 NaCl–0.74 LiCl	670	−17.9	−10.1	−27.4
0.50 NaCl–0.50 KCl	720	−25.9	−15.8	−41.6

The conclusion, based on previously reported data, that uranyl(VI) complexation decreases with increasing uranyl(VI) concentration is not valid.

In the electrolytic codeposition of uranium and plutonium oxides, the resulting plutonium enrichment is dependent upon a number of variables, including temperature, current density, duration of electrolysis, and the oxygen-to-chlorine ratio of the sparge gas. Plutonium enrichment factors as high as 13.5 have been achieved in the codeposited oxide product[46,47] by optimizing these variables. In one experiment, 5% of the uranium and 68% of the plutonium were codeposited, yielding a product containing 14 wt.% plutonium dioxide. An indication of the behavior of rare-earth fission products was provided by a decontamination factor of 6 for promethium, relative to plutonium.

Recent results[48] have shown that a fine-grained form of plutonium dioxide can be prepared by electrolysis of a molten chloride solution of plutonium trichloride during sparging with an oxygen-chlorine mixture. Successful depositions were obtained from a LiCl-KCl solvent at 550°C, using a 60% oxygen–40% chlorine sparge, and from a CsCl melt at 700°C, using an 80% oxygen–20% chlorine sparge. The electrodeposition reaction is believed to involve reduction of Pu(V) and Pu(VI) intermediates, which have been tentatively identified by spectrophotometric methods in molten-salt solutions of Pu(III) and Pu(IV) sparged with oxygen or oxygen-chlorine mixtures.[48]

Gaseous Low-Decontamination Process for Uranium Dioxide

Gaseous oxidation-reduction reactions are being utilized at Atomics International for low-decontamination processing of uranium oxide reactor fuels by remote techniques. The fuel cycle consists of pulverizing the refractory uranium dioxide by alternately oxidizing with air or dilute oxygen at 200 to 600°C and reducing with hydrogen at 600°C. The powdered uranium dioxide product is refabricated by conventional cold-pressing and sintering techniques.

This process has been demonstrated on a kilogram scale, using unirradiated urania-fissia* pellets simulating total burnups of 0 to 100,000 Mwd per metric ton of uranium (0 to 10 at.%).[54] The demonstrations involved five processing and refabrication cycles, with fissia added to simulate a burnup of 2% for each cycle. The effects of increasing fissia concentration in the fuel on the processing and refabrication operations were evaluated, the densities of the refabricated pellets were compared, and the fission-product element removals were determined. Although some plant prototype equipment was used, the operations were not conducted remotely.

In the oxidation step, $\frac{3}{8}$-in. fuel pellets in three stainless-steel baskets were heated inductively using a stainless-steel susceptor, while air at atmosphereic pressure was passed over the charge at a rate of about 2 cu ft/hr. The oxidation started at about 325 to 375°C, and the heat of reaction raised the temperature to approximately 425 to 450°C. Reduction of the resultant U_3O_8 to UO_2 was conducted at 600 to 700°C in the same equipment; hydrogen was used at atmospheric pressure and at a flow rate of 8 to 10 cu ft/hr. Although the oxidation and reduction reactions can both be carried out at higher temperatures to achieve faster rates, lower temperatures produce a finer product that is more suitable for pellet refabrication.

When the uranium dioxide powder had passed through sufficient reductions and oxidations, fissia powder was added to simulate an additional 2% burnup. The fissia was blended with the uranium dioxide just prior to cold pressing and sintering. Polyvinyl alcohol (PVA) was then added as a binder (1 wt.%), and the mixture was dry blended for 1 hr. Twenty weight percent distilled water was added in increments, and the mixture was regranulated. After the addition of $\frac{1}{2}$% zinc stearate as a die lubricant, the powder was cold pressed at 80,000 psi. The pellet charge was slowly introduced into the sintering

*The term "fissia" refers to compounds of stable isotopes representing fission-product elements existing in irradiated oxide fuel.

furnace at 1150°C and finally sintered at about 1750°C.

In all the cycles the presence of fissia had little or no effect on fabrication operations, and excellent pellets were obtained. The densities and grain sizes of the product are summarized in Table III-3. No fissia constituents were removed by this process except cesium, which was completely removed. It was concluded that uranium losses on a plant scale would be limited to less than 2 or 3% per processing cycle.

Work is also continuing at Atomics International on processing studies, on a 100-g scale, of uranium dioxide irradiated to burnups as high as 15,000 Mwd per metric ton of uranium.[55]

Carbide Fuel Processing

Development of three schemes for processing irradiated uranium monocarbide fuels has continued at Atomics International.[55–57] The first, to which the major effort is being devoted, consists of a carbide-oxide-carbide cycle. The fuel is first oxidized by oxygen, air, or carbon dioxide at about 400 to 600°C, and the resulting oxide is then reconverted to uranium monocarbide by carbothermic reduction at or above 1300°C. In the second process, uranium monocarbide is converted to a mixture of uranium nitride and carbon by reaction with nitrogen at about 900°C. This mixture is reconverted to uranium monocarbide by heating in vacuum above 1500°C. The uranium monocarbide in the third process is electrolyzed in a LiCl-KCl bath, depositing dendritic uranium metal on a molybdenum cathode. This deposit is dissolved in hot mercury and is subsequently converted to the monocarbide by distillation of the mercury in a propane atmosphere. Only the third process produces significant fission-product decontamination. The other two processes are mainly refabrication procedures that permit reenrichment of the fuel and repair of irradiation damage.

Processing by the Carbide-Oxide-Carbide Cycle

The decladding and oxidation steps of the carbide-oxide-carbide cycle have been investigated by using 100-g quantities of uranium monocarbide irradiated to burnups as high as 15,000 Mwd per metric ton of uranium.[58] The carbide was oxidized by air:

$$UC + 2O_2 \rightarrow UO_2 + CO_2 \quad (1)$$

Since theoretical densities are 13.63 g/cm^3 for uranium monocarbide and 10.97 g/cm^3 for uranium dioxide, the volume change on oxidation causes the fuel to fragmentize. This effect has been exploited successfully for removing oxide fuels from metallic cladding, and it is expected that carbides can be decanned by the same technique. The product from the decladding procedure is further oxidized in air to form U_3O_8, which is then reduced with hydrogen to form uranium dioxide:

$$3UO_2 + O_2 \rightarrow U_3O_8 \quad (2)$$

$$U_3O_8 + 2H_2 \rightarrow 3UO_2 + 2H_2O \quad (3)$$

Table III-3 DESCRIPTION OF METALLOGRAPHIC SPECIMENS OF UO_2 PELLETS[54]

Sample No.	Identification	Density, % of theoretical density		Grain size,* μ	
		Geometric	H_2O displacement	Average†	Range
MCW-1	Original Mallinckrodt normal UO_2	93.4	94.0	5	5–10
ETB-I	Refabricated normal UO_2	94.8	97.4	20	10–25
ETB-II	Simulated 2% burnup	93.4	95.6	15	10–25
ETB-III	Simulated 4% burnup	91.2	92.5	15	13–23
ETB-IV	Simulated 6% burnup	97.8	99.5	13	10–20
ETB-V	Simulated 8% burnup	97.0	99.3	13	13–25
ETB-VI	Simulated 10% burnup	99.2	100.6	13	13–23

*Converted from typical correlations, such as ASTM-10 = 0.0004 in., ASTM-9 = 0.0006 in., and ASTM-7.5 = 0.0010 in.

†The size of the majority of grains.

Continued alternate treatments with oxygen and hydrogen have been found to diminish further the particle size to an optimum for reconversion to the carbide:

$$UO_2 + 3C \rightarrow UC + 2CO \quad (4)$$

It had been shown previously[59] that the oxidation behavior of unirradiated uranium monocarbide is dependent upon the history of the material. Freshly arc-melted material is relatively resistant to oxidation, whereas "reactive" material that has been exposed to water vapor ignites in oxygen at about 300°C. It was therefore of interest to determine whether irradiation of the carbide would convert it to a reactive form. To simulate the decladding step, pieces of the irradiated carbide were placed in a metal capsule, and air at pressures of 2 to 18 in. Hg abs was admitted to the fuel, which was heated to about 225°C. The reaction rate increased thirtyfold between air pressures of 2 and 18 in. Hg abs. This treatment caused the uranium monocarbide to pulverize, but very little oxidation occurred. This product, along with additional small pieces of uranium monocarbide, was then subjected to one oxidation-reduction cycle. Complete conversion of the material to uranium dioxide was achieved, with over 83% of the product passing through a 200-mesh screen. During the oxidation step, ignition occurred at about 300°C and indicated that the material was a reactive form of the carbide. The product resulting from the single oxidation-reduction cycle was judged to be suitable for reconversion to the carbide without further processing. Fission-product and plutonium decontamination factors for the processed product were less than 2.5 in all cases and were near unity in most instances.

As an alternative to Reaction 1, oxidation by means of carbon dioxide has been considered for the conversion of uranium monocarbide to the oxide:[60]

$$UC + 2CO_2 \rightarrow UO_2 + 2CO + C \quad (5)$$

Reaction 5 has been studied by thermogravimetric methods using aged or reactive uranium monocarbide for the most part, although freshly arc-melted material was used in a few experiments.[60] The reactive carbide began to react at about 350°C, and between 375 and 500°C the overall rate equation for the reaction was

$$\frac{dx}{dt} = k(1 - x)\,(P_{CO_2})^{0.7} \quad (6)$$

where x is the fraction of the reaction completed at time t, k is a first-order rate constant, and P_{CO_2} is the carbon dioxide pressure. Over this temperature range the activation energy for the reaction was 25 kcal/mole. As the temperature was increased further, ignition occurred at about 525°C. Above this temperature the rate expression in Eq. 6 no longer holds. At temperatures above about 670°C, the free carbon product in Reaction 5 is oxidized; thus the overall reaction becomes

$$UC + 3CO_2 \rightarrow UO_2 + 4CO \quad (7)$$

However, this reaction occurs in a stepwise manner, most of the carbon being oxidized after oxidation of the uranium carbide is complete. The freshly arc-melted uranium monocarbide proved to be unreactive toward carbon dioxide, even at 600°C. It was converted to the reactive state, however, by four days of exposure to air saturated with water vapor.

Use of carbon dioxide instead of oxygen or air may result in easier control of the oxidation reaction, since less heat is generated and the temperature dependence of the rate is greater. The product of the carbon dioxide reaction appears to be suitable for reconversion to uranium monocarbide.

Additional results[57] have been reported by Atomics International on the use of carbon instead of hydrogen for the reduction of U_3O_8 to UO_2. At temperatures of 835 to 930°C, reduction of U_3O_8 to UO_2 by carbon resulted in initial weight losses of 5.8 mg/min at 835°C and 26.3 mg/min at 930°C. The temperature dependence of the rate corresponds to an activation energy of 42 kcal/mole. At higher temperatures, reductions of UO_2 to UC occurred at rates that were correlated with the rate equation

$$kt = 2\left[\frac{1}{(1 - x)^{1/2}} - 1\right] \quad (8)$$

where x is the fraction of the reaction completed at time t and k is the rate constant. The rate constants (min^{-1}) were 0.0157 at 1320°C and 0.267 at 1560°C. The activation energy was 70.6 kcal/mole.

Kilogram-level scale-up studies have continued on the carbothermic method for reconverting uranium oxides to the carbide.[55–57]

The preparation of hypostoichiometric (carbon-deficient) uranium monocarbide with complete removal of oxygen has proved to be no more difficult than the preparation of the stoichiometric material.[56] The optimum finishing temperature for the reaction is about 1750°C.

Preparation of Uranium Metal from U_3O_8

Uranium metal has been prepared by the carbothermic reduction of U_3O_8 in a uranium dioxide crucible[56] at 1850°C. For fuel-processing applications of this procedure, it is considered that the product would be suitable for reconversion to uranium carbide or uranium dioxide, and it is expected that considerable fission-product decontamination would result from the drossing effect.

Electrolytic Processing of Uranium Carbide Fuel

Substitution of molten cadmium for a solid molybdenum cathode in the electrolytic processing scheme for uranium carbide fuels has been investigated further.[56] Using a uranium monocarbide anode and a LiCl-KCl-UCl_3 bath, an improved cathode efficiency resulted from a reduction in the current density:

Current density, amp/dm²	Cathode efficiency, %
10.6	15
3.5	34
1.8	36

Extrapolation of the potential to zero current gave a value of 1.06 volts.

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Section

IV

Reactor Fuel Processing

Waste Disposal

Liquid-Waste Treatment by Ion Exchange and Foam Separation

Ion Exchange

At Oak Ridge National Laboratory (ORNL), a scavenging ion-exchange process[1–4] is being developed for decontaminating the large volumes of slightly contaminated water which are produced in processing of nuclear fuels. This process employs a head-end treatment step that involves precipitation with sodium hydroxide of a portion of the activity, clarification of the water in a gently agitated sludge-column clarifier, and a filtration of the effluent from the clarifier unit. The clarified and filtered effluent is then passed through a carboxylic-phenolic resin for sorption of Cs^{137} and Sr^{90}.

In laboratory and pilot-plant tests, water clarification techniques[3,4] are being studied in an effort to reduce the total hardness of the effluent from a clarifier unit. The reduction of the hardness in the effluent stream to the clarifier increases the quantity of solids removed by the sludge blanket and reduces the burden on the polishing filters. Complete precipitation of the hardness ions is hindered by the presence of excessive amounts (up to 3 ppm) of phosphate in ORNL low-level-activity process wastes. In pilot-plant tests with ORNL low-level-activity plant waste, 0.005*M* Na_2CO_3 was successfully used to precipitate calcium from wastes containing up to 3 ppm phosphate and resulted in a decrease in the hardness ions (from 100 to 20 ppm) of the effluent leaving the clarifier.

Although the removal of Sr^{90} from ORNL low-level-activity plant wastes was not affected by the addition of 0.005*M* Na_2CO_3, the use of sodium carbonate[4] has a pronounced effect on the removal of Cs^{137}. The addition of 0.005*M* Na_2CO_3 doubles the concentration of sodium ion present in the waste solution and reduces the capacity of the ion-exchange resin for cesium by 50% at the 0.1% breakthrough level. The effect of varying amounts of hardness ions on the cesium capacity of an ion-exchange column was also investigated. High hardness content in a radioactive contaminated waste stream reduces the capacity of an ion-exchange resin for cesium and strontium because of the increased competition for resin sites. In tests in which the calcium concentration of the influent to the ion-exchange column was increased from 0 to 8.5 and 43 ppm (as $CaCO_3$), the cesium breakthrough capacity at 0.1% was reduced from 1850 to 1350 and 520 bed volumes, respectively.

ORNL has also been investigating the use of gibbsite,[3,5] an aluminum hydroxide, as a sorbent for strontium. When gibbsite is heated above its decomposition temperature of 150°C, it becomes a highly selective sorbent for strontium in neutral and alkaline media. Measurements of the surface area showed that the product obtained on heating gibbsite increased in area from about 0.3 m^2/g for the unheated gibbsite to over 200 m^2/g after heating. In recently reported ORNL work,[3] the capacity of the heat-treated gibbsite to sorb cesium and strontium without any interfering ions present was determined. The capacity of the heat-treated gibbsite is approximately 4 meq/100 g for cesium and 12 meq/100 g for strontium. The amount of cesium sorbed from solution remained relatively constant over the *p*H range from 6 to 10.

Cesium could be readily leached from the heat-treated gibbsite with an elutriant solution (*p*H 8) that contained 0.01*N* $NaNO_3$. The passage

of sodium ions equivalent to 1.7, 3.3, and 23 times the concentration of cesium sorbed on the column resulted in removal of 57, 83, and 96%, respectively, of the cesium.

It was more difficult to remove the strontium than the cesium from the heat-treated gibbsite with elutriant solutions (*p*H 8) that contained sodium nitrate. In these tests, when the 0.01*N* $NaNO_3$ was no longer effective for desorbing strontium, the concentration of the sodium nitrate in the elutriant solution was increased stepwise from 0.01*N* to 5*N*. The passage of sodium ions (0.1*N* $NaNO_3$) equivalent to over 100 times the concentration of strontium on the sorbent resulted in only 50% of the strontium being desorbed. The passage of sodium ions (1*N* $NaNO_3$) of over 730 times the strontium concentration desorbed 77% of the strontium. The passage of sodium ions (5*N* $NaNO_3$) equivalent to about 7000 times the concentration of strontium on the sorbent was required for removal of over 95% of the strontium.

The difficulty with which strontium was desorbed is evidence of a strong bond between the sorbent and strontium. However, the strontium was desorbed quite readily when the *p*H of the sodium nitrate solution was dropped below neutral.

Several hydrous oxide minerals of iron and aluminum were heated to 500°C to test whether they would show properties favorable for the sorption of strontium.[4] Heat-treated limonite with a surface area of 93.2 m^2/g appeared to be the best of those tested. Like gibbsite, the heated limonite removes strontium best from alkaline solutions. The limonite sorbed 99.6% of the strontium from 0.1*N* $NaNO_3$ containing $1 \times 10^{-5} M$ Sr^{2+}. The reaction reached equilibrium in about 4 hr. Limonite showed a relatively high affinity for strontium even prior to heating, but the heat-treatment produced a superior product. The high reactivity of limonite in the natural state is probably due to the initially high surface area (20.8 m^2/g).

Decontamination of Purex Tank-Farm Condensate at Hanford

At Hanford, experiments were continued in the Micro Pilot Plant (MPP) to develop an ion-exchange process for decontaminating Purex tank-farm condensate.[5,6] Two ion-exchange runs[6] were made to examine the removal of ruthenium from this condensate waste. During the early portion of one run, about 99% of the ruthenium was removed by passing a Purex tank-farm condensate that had been steam stripped through a mixed bed resin (Illco TM-1).* The steam-stripped condensate had a *p*H of 7.3 and contained 20 ppm ammonia, 5 ppm sodium, 25 ppm nitrate, and 32 ppm nitrite. When the ion-exchange bed had become saturated with nitrate and nitrite ions, the removal of ruthenium decreased, but 90% of the ruthenium continued to be removed for the remainder of the run (1700 column volumes). Strontium concentration in the effluent was maintained at about its MPC_w value during the entire run, a decontamination factor of 35 being achieved. During the last 200 column volumes of the run, carbon dioxide gas was added to the steam-stripped condensate feed to lower the *p*H from 7.3 to 4.5. At the lower *p*H the decontamination factor for strontium increased to 350. Cesium was removed with a decontamination factor greater than 1000 for about 500 column volumes treated. At this point the concentration of cesium in the effluent began to increase. This coincided with the appearance of ammonia and sodium ion in the column effluent.

In the other run a steam-stripped condensate feed was initially passed through a cation-exchange bed and then through a bed of weak-base anion resin (Nalcite WBR† in the hydroxyl form). The overall removal for ruthenium varied from 80 to 94% during the entire run (4800 column volumes). The high degree of removal of ruthenium which had been obtained with the strong-base anion resins was not achieved with the weak-base anion resin.

Conference on Treatment of Radioactive Wastes with Mineral Exchangers

The report on the proceedings[7] of a conference sponsored by AEC on the use of inorganic exchange materials for radioactive waste treatment has become available. Topics for discussion included: (1) use of various natural mineral materials for waste treatment and disposal purposes, (2) programs being conducted to obtain physicochemical and radiological data on the reactions of these materials with radionuclides, and (3) additional studies

*A product of Illinois Water Treatment Co., Rockford, Ill.

†A product of Nalco Chemical Co., Chicago, Ill.

required to develop further understanding of the mechanisms and interrelations involved in mineral exchange.

Conversion of High-Level-Activity Wastes to Solids

The AEC has announced[8] that, in late 1963, a demonstration fluidized-bed calcination run with high-level-activity liquid wastes is planned for the Waste Calcining Facility[2] (WCF) at the National Reactor Testing Station (NRTS) in Idaho. Actual plant wastes that have accumulated from the chemical processing operations at the NRTS since 1953 will be used as feed materials in this radioactive demonstration run.

The report on the proceedings[9] of the Third AEC Meeting on Calcination and/or Fixation of High-Level Wastes in Stable, Solid Media has been issued by the AEC. Results of laboratory work, cold engineering studies, and the design of hot pilot-plant demonstration facilities were presented and discussed in detail.

Spray Calcination

Hanford is continuing to study radiant-heat spray calcination[2] for the treatment of Purex high-level-activity aqueous wastes. In radiant-heat spray calcination, the feed solution is sprayed into the top of a heated column that is maintained at 700 to 750°C. Spray droplets are converted to solids, and some salt decomposition is achieved by radiant energy from the heated column. The dried residue falls into a melt pot. Further decomposition and melting of the dried residue take place continuously in a melt pot which is maintained well above the melting temperature of the dried residue, typically 750°C, and which is used to effect a reduction in volume of the residue. A radiant-heat spray-calciner run[6] was made in which sugar was added to full plant-level-activity concentrated acid waste (1WW) to test its effectiveness in reducing the volatilization of ruthenium from acid wastes. The addition of sugar (50 g/liter) to the 1WW feed did reduce the volatilization of ruthenium. The decontamination factor for ruthenium when the spray calciner and melt pot were used increased from 5 to 30. The cumulative decontamination factors for ruthenium which were achieved by the various components in the spray calciner and off-gas treatment installation were as follows:

Calciner component	Cumulative decontamination factor
Spray calciner and melt pot	30
Condenser	1.5×10^5
Caustic scrubber	1.2×10^6
Electrostatic bubble scrubber	2.4×10^6
Silica gel and charcoal beds	1.7×10^7
Cambridge absolute filters	$\sim 3.4 \times 10^9$

The installation of a semiworks-scale radiant-heat spray calciner[6] for use with nonradioactive feed solutions was also completed at Hanford. A schematic diagram of the equipment is shown in Fig. IV-1. The calciner (constructed of $\frac{1}{4}$-in. Inconel X plate) is 10 ft in length and 18 in. in diameter and has a nominal capacity of 20 gal/hr. It is contained within a resistance-heated furnace that is divided into three independently controlled zones. The feed is introduced through pneumatic atomizing nozzles.

A standard cyclone separator and a filter are used to separate the calcined particles from the off-gas stream. The filter unit contains fourteen 10- to 100-μ pore size alumina filter elements. Each filter element has a filtration area of 3 sq ft. A pneumatic blowback system is used to remove the calcined particles from the filters.

The condensables are removed from the off-gas stream in a surface condenser. The noncondensables pass through a packed tower where the gases are scrubbed with a caustic solution to remove residual oxides of nitrogen. The remaining gases pass through a steam jet, which maintains the entire system under a slight vacuum, and are discharged to the atmosphere via a stack. The calcined solids are collected at three points: in pots below the reactor and below the cyclone and on the filter elements. At present there is no heating equipment installed to melt the calcine as it is collected.

An electrostatic precipitator that was developed at Hanford for removing radioactive particulate matter from off-gas streams in connection with the radiant-heat spray-calcination program is described in a report by Allemann and Upson.[10] This new type of electrostatic

precipitator (Fig. IV-2) achieves high efficiency (99 to over 99.9%) at reasonably low pressure drop (1 to 2 in. H_2O). It has been named the "electrostatic bubble scrubber" because its effectiveness is obtained by bubbling gas laden with electrostatically charged particles through a liquid of opposite charge. The dust-laden gas stream is first passed through a corona discharge region, which imparts an electrical charge to each particle, and then through holes provided to break up the gas stream into bubbles. The bubbles are then quickly passed through a conducting liquid (such as water) which is at ground potential. In this manner all the particles are brought into close proximity to the water surface and are strongly attracted to it by the resulting high potential gradient. Once in contact with the liquid surface, the particles are dissolved or dispersed in the liquid and thus do not build up to cause arcing, as in a conventional electrostatic precipitator.

Pot Calcination

ORNL is continuing its investigation of the pot-calcination process[3,4,11] for converting high-level-activity wastes to solids. It is being studied on both a laboratory and engineering scale with synthetic Purex, Darex, and TBP-25 wastes to provide design information for the construction of a pilot plant at Hanford. The first phase of the program is concerned with direct calcination processes, where melting does not occur and little or no additives are combined with the wastes. In the second phase, enough additives are combined with the waste for the subsequent formation of a glasslike material in which the fission products are fixed. (Calcination by radiant-heat spray and possibly by rotary-ball calciners is also to be demonstrated in this pilot plant.[3])

In laboratory-scale experiments the possibility of retaining all the sulfate present in

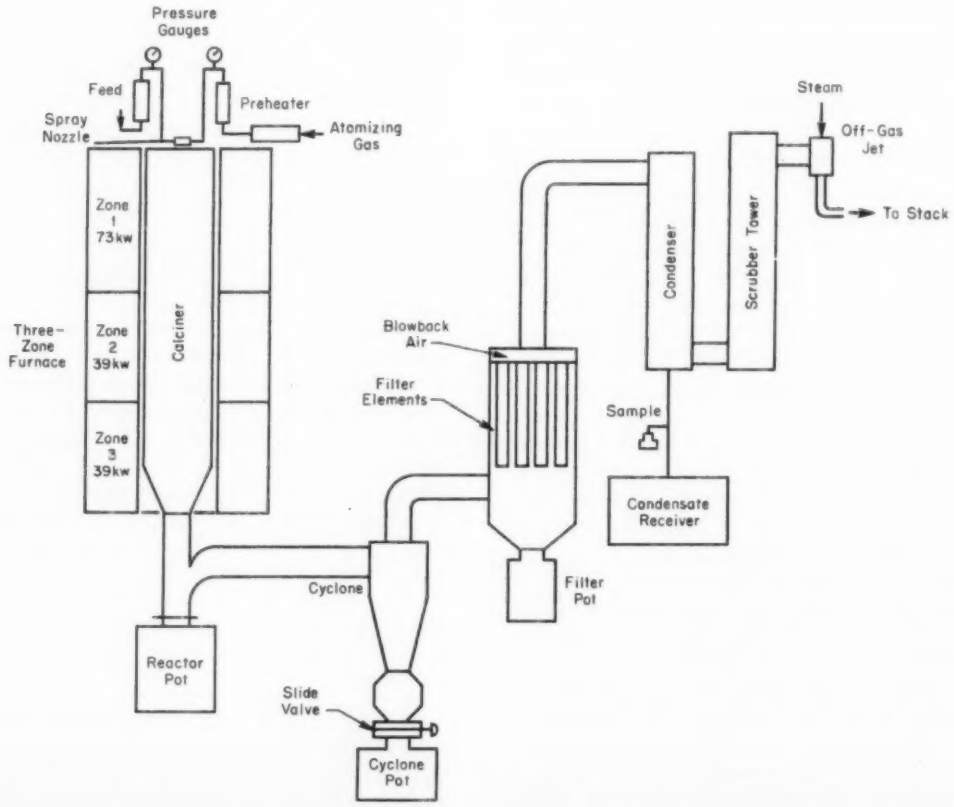

Fig. IV-1 Cold semiworks radiant-heat spray-calciner equipment arrangement.[6]

high-sulfate Purex-waste solutions in the solid formed when the latter is a glass was investigated.[3,4] Glasses have been formed from this waste solution after volatilizing part or all of the sulfate or by quenching small batches of melt. Slow cooling of large batches that lost little sulfate invariably resulted in the formation of crystalline materials. Glasses are more desirable than crystalline products because of their smaller microsurface areas, greater tendency toward homogeneity, and property of softening gradually with increasing temperature. A crystalline solid may, however, be satisfactory, depending upon its insolubility, homogeneity, and melting characteristics. In general, thermal conductivity is somewhat greater for crystalline solids than for glasses.

Sulfate volatility from melts containing 39 wt.% simulated Purex-waste oxides was investigated as a function of mixtures of Na_2O, CaO, and P_2O_5 content. All melt compositions investigated lost some sulfate at temperatures as high as 50 to 100°C above the softening point (825 to 1000°C). In general, the volatility decreased with increase of either Na_2O or CaO relative to P_2O_5, but no simple correlation was indicated. Softening temperatures were increased with an increase in CaO content. Ceramic solids were obtained but no true glasses. Attempts to produce glasses by addition of varying combinations of Al_2O_3, PbO, BaO, and B_2O_3 to simulated Purex waste containing phosphite were unsuccessful.

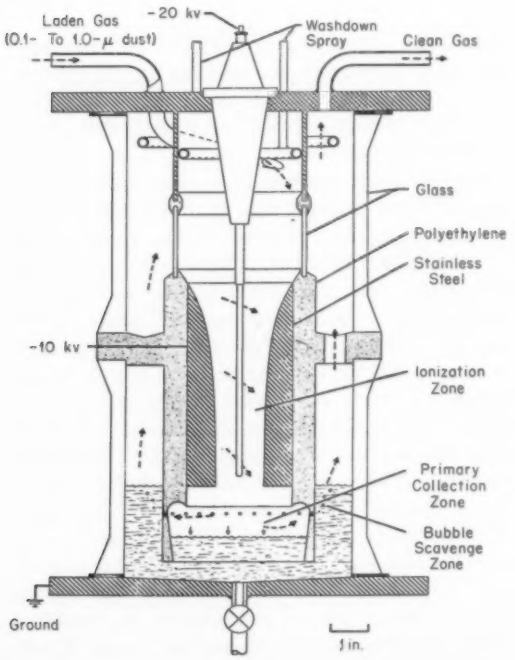

Fig. IV-2 Electrostatic "bubble scrubber."[10]

Wheeler and Buckham[12] at the Idaho Chemical Processing Plant (ICPP) report on the design of a pilot-plant facility for the radioactive demonstration of the pot-calcination process. This facility was designed in collaboration with ORNL and was to be constructed at ICPP. However, it was later decided to build the facility at the Hanford Atomic Products Operation (HAPO). The report summarizes the scope and the objectives of this radioactive demonstration program, discusses in detail the engineering process flow sheet, presents the design basis for the major process equipment, and gives cost and schedule information as they pertain to the initially planned installation at ICPP.

Survey of Rock-Salt Sites in the United States for Storage of Radioactive Wastes

A thick salt bed for the storage or disposal of radioactive waste products is viewed with favor because salt, which is relatively plastic, seals itself and eliminates the likelihood that the material stored within it will come in contact with ground water. Salt mines,[13] for example, are considered a most promising place for the storage of packaged, calcined high-level-activity wastes.

The U. S. Geological Survey has compiled a summary report[14] based on available literature on the rock-salt deposits of the United States. Information on the geology of salt and the distribution, thickness, and depth below the surface of all known rock-salt deposits of the United States was assembled so that possible sites for storage or disposal of radioactive waste in salt beds may be correlated with plans for the geographic location of power reactors and fuel-element processing plants. Salt deposits are found in 24 states. Some of the deposits have a lateral extent of several hundred miles. Rock-salt deposits that are bedded like those in Michigan and New York, and those which are plastically deformed masses as in the case of the Gulf Coast salt domes, are discussed in the report. Because it is soluble, bedded salt does not commonly occur at the surface.

Recovery of Fission Products

As part of its Waste Management Program,[15] Hanford is investigating ion-exchange and solvent-extraction processes for the extraction of long-lived heat-producing fission products from various Purex-plant waste streams. In laboratory experiments the effects of particle size, flow rate, and temperature on strontium loading of columns of Linde 4A zeolite were studied.[6] A feed solution containing 0.20*M* $NaNO_3$, 0.035*M* $Sr(NO_3)_2$, 0.010*M* $Ca(NO_3)_2$, and added Sr^{85} tracer was used in the experiments. This solution simulates the strontium product solution from the solvent-extraction process that is under development at Hanford for the recovery of strontium.[16]

The effect of particle size on the strontium breakthrough curves is shown in Fig. IV-3. These experiments were conducted at 80°C and a flow rate of 12 column volumes per hour. In the course of these experiments, it was found that the breakthrough curve for strontium loading on 30- to 35-mesh Linde 4A zeolite is nearly the same as for that for the commercially available 20- to 50-mesh Linde 4A zeolite (not shown in Fig. IV-3). The effect of the flow rate and temperature on the strontium breakthrough curve for 30- to 35-mesh particle size Linde 4A is shown in Fig. IV-4. These experiments were conducted at flow rates of 3 and 12 column volumes per hour and at temperatures of 25 and 80°C. The results of these latter experiments show that the loading rate was increased without sacrificing strontium capacity when the temperature was increased from 25 to 80°C. The amount of strontium adsorbed at the various column throughput values for each of the breakthrough curves shown in Figs. IV-3 and IV-4 is listed in Table IV-1. Other experimental data[6] indicate that large particle sizes such as 1/16-in. pellets or 8- to 12-mesh beads would require very slow flow rates or considerable recycle to avoid high strontium losses.

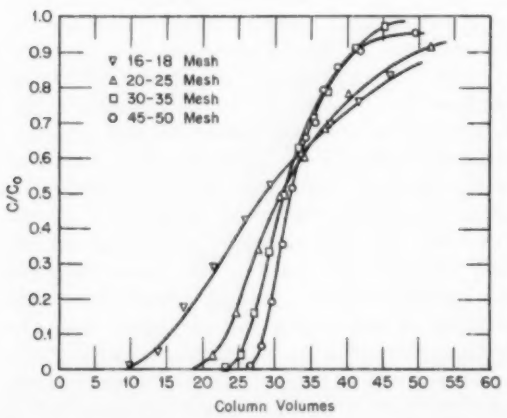

Fig. IV-3 Effect of particle size on strontium breakthrough curve with Linde 4A zeolite.[6]

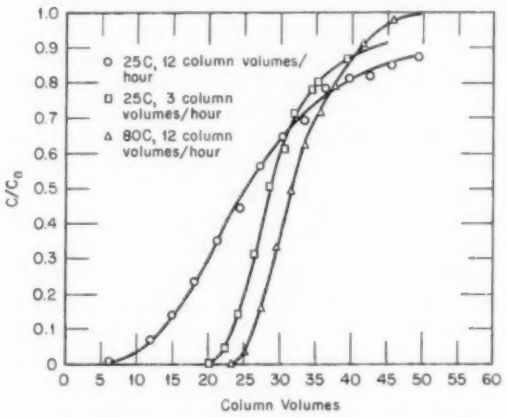

Fig. IV-4 Effect of flow rate and temperature on strontium breakthrough curve with Linde 4A zeolite.[6]

The removal, purification, and recovery of cesium[6,15] by clinoptilolite from formaldehyde-treated Purex acid wastes (FTW) continues to be studied at Hanford. The current process flow sheet, which was given in a previous issue of *Reactor Fuel Processing*,[16] is repeated here for convenience. Clarified FTW is passed through a bed of clinoptilolite which adsorbs cesium, some sodium, and slight amounts of other radioactive cations. The sodium is eluted from the column with oxalic acid solution followed by a water wash and subsequent elution of the hydrogen ion with ammonium hydroxide. The cesium is then eluted with ammonium carbonate solution. The separation of cesium from Zr^{95} and Nb^{95} was determined in a run at greater than tracer-level activity. A simulated FTW that was composed of 14% actual Purex 1WW was used for feed. Decontamination factors for cesium from Zr^{95} and Nb^{95} were 700 and 70,

respectively. The decontamination factor for Nb^{95} is a factor of 10 greater than that obtained in previously reported[17] laboratory tracer-level-activity experiments. The improved decontamination factor is believed to result from the use of oxalic acid as an elutriant for removing sodium from the column instead of the nitric acid that was used in the tracer-level-activity experiments. During the loading cycle the concentration of cesium in the effluent reached 10% breakthrough at 60 column volumes compared with 77 column volumes for the tracer-level-activity experiments.

Table IV-1 STRONTIUM LOADING OF LINDE 4A ZEOLITE[6]

Experimental conditions			Strontium loading, meq/g				
			Column volumes				
Flow rate, column volumes per hour	Temp., °C	Particle size, mesh	30	35	40	45	50
12	80	16–18	2.10	2.29	2.38	2.49	2.60
12	80	20–25	2.33	2.53	2.65	2.72	2.77
12	80	30–35	2.43	2.61	2.69	2.71	2.76
12	80	45–50	2.47	2.70	2.79	2.80	2.86
12	25	30–35	1.98	2.10	2.18	2.24	2.34
3	25	30–35	2.31	2.42	2.48	2.50	

Packaging of Fission Products

Engineering development studies on the packaging of fission products using inorganic zeolites were continued at Hanford.[6,18] Synthetic zeolites of high capacity and low selectivity (such as Linde 13X) are being considered as solid media on which to sorb Cs^{137} and Sr^{90} for shipping or storage. The total quantity of fission-product activity in the container and the size of the container will be controlled, to a large extent, by allowable equilibrium temperatures.[6] Both the container wall temperature and maximum internal temperature must be considered in the design of the container. Permissible wall temperature is based on such factors as (1) external corrosion of the container in air or water over a long period of time, (2) strength and stability of construction materials, and (3) ease of mechanical handling. Available data on corrosion, mechanical stability, and strength indicate that ease of mechanical handling is the main criterion for establishing the permissible wall temperature. On this basis a temperature of 600°F is about the limiting value. Above this temperature, difficulties arise due to thermal expansion and contraction of handling mechanisms, thermal shock during decontamination, and difficulty in heat removal during transport in shielded casks if the latter is necessary.

Internal temperatures as high as 1300°F can be tolerated in the zeolite bed without adverse effects on stability or product retrieval. The highest temperature would, of course, occur along the center line of a cylindrical container. Greater capacity per unit length can be attained by using a container of annular cross section, cooled from both inner and outer surfaces.

Figure IV-5 shows calculated centerline and surface temperatures for cylindrical containers

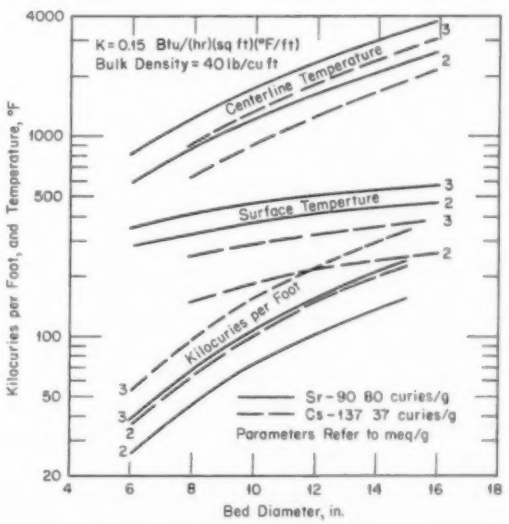

Fig. IV-5 Equilibrium temperatures and capacities for packages of Sr^{90} and Cs^{137} (Ref. 6).

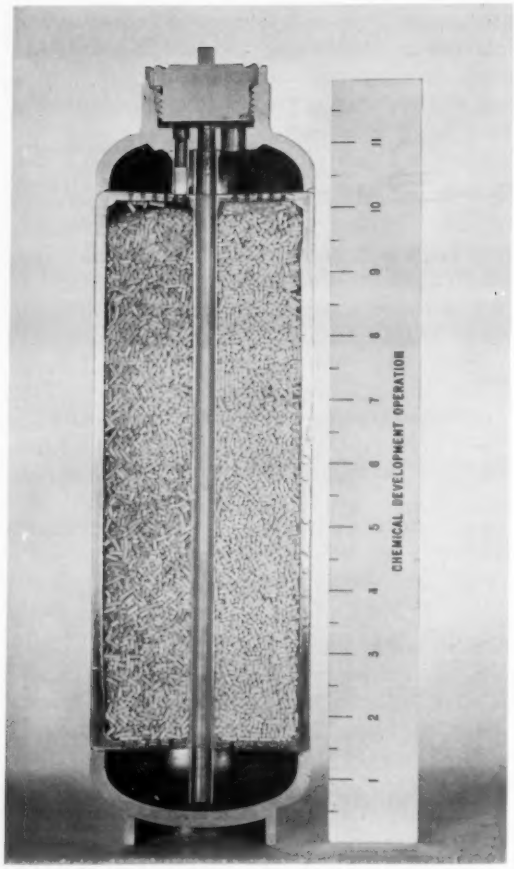

Fig. IV-6 Model of conceptual fission-product container.[6]

of various diameters for Sr^{90} and Cs^{137} loadings of 2 and 3 meq/g. (On a milliequivalent basis, Sr^{90} and Cs^{137} have approximately identical heat output.) Temperatures shown for Cs^{137} take into account that portion of the gamma energy from Cs^{137} decay which escapes conversion to heat within the container. Cooling is assumed to be by natural convection and radiation (emissivity = 0.4) from container sides to surroundings at 70°F ambient temperature. Helium is used in interstitial volume to provide an effective thermal conductivity of 0.15 Btu/(hr)(sq ft)(°F/ft) in the bed.

One possible concept of a fission-product container is illustrated in Fig. IV-6, which shows a section of a one-quarter-scale model cylindrical container.

Structural Integrity of Shipping Containers for Radioactive Materials

The Franklin Institute, Philadelphia, has issued its first report[19] on a research program, the objective of which is to develop quantitative methods for assessing the structural integrity of shipping containers[20] for radioactive materials. The overall program encompasses the following:

1. Study of transport operations and container construction
2. Study of small-scale models, vehicle rigging dynamics, and container fire damage
3. Experimental investigation of large-scale models, full-size containers, and full-size vehicles

The work discussed in this report is concerned primarily with item 1 of the program. It summarizes the results of a study of available information concerning rail and highway transportation as well as design and construction features of a number of existing containers. The major part of the work covered in this report was carried out between April 1960 and June 1961.

Corrosion in Waste Processing

A recent report from the ICPP covers the design of a proposed pilot-plant facility for radioactive demonstration of the pot-calcination process for radioactive liquid high-level wastes.[12] Although most of the report is related to general process design considerations and descriptions of process and equipment, a small section on proposed construction materials is included. Figure IV-7 is a schematic drawing of the relation of four major equipment items: evaporator, fractionator, calciner, and calciner condenser. The unit is intended to handle a variety of process wastes including those from the Darex process (20 to 300 ppm chloride anticipated) and Purex wastes (115 ppm fluoride anticipated).

Type 304L stainless steel was selected as the construction material for much of the equipment, whereas titanium was selected for the evaporator, the calciner condenser, the 4-in.-diameter line between the evaporator and fractionating column, and the fractionating column. The factors influencing the selection of titanium

were the following: (1) available corrosion data indicate that stainless steel has a much shorter life expectancy than titanium for aluminum nitrate and stainless-steel nitrate wastes, (2) hexavalent chromium and trivalent iron in Darex and electrolytic dissolver wastes are known to promote excessive intergranular corrosion of stainless steels, and (3) although certain stainless steels can be made resistant to fluoride corrosion by proper annealing, this is difficult to accomplish completely and satisfactorily in the case of vessels as large as some of those designed for this facility. Provisions have been made for adding a complexing agent such as aluminum nitrate, boric acid, or zirconyl nitrate to the condenser and fractionating column, if necessary, to keep vessel corrosion due to fluorides within tolerable limits.

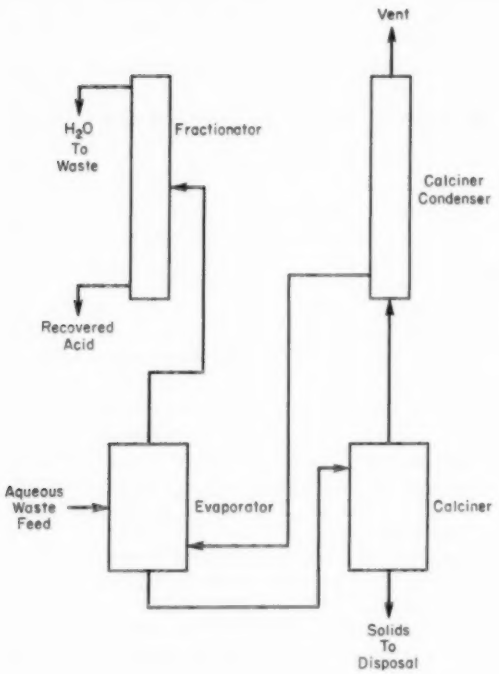

Fig. IV-7 Schematic of principal equipment items in proposed pot-calcination process. (Adapted from Ref. 12.)

For several years the ICPP has been monitoring corrosion in its 30,000- and 300,000-gal waste-storage tanks. This has been accomplished by the insertion of various types of corrosion coupons. The results of these evaluations were recently included in a report released by Idaho.[21] Four different types of wastes are isolated at the plant and stored in separate waste vessels: (1) the acid-deficient nitrate-containing wastes from the first-cycle hexone 25 process, (2) aluminum nitrate–nitric acid wastes from the first-cycle TBP-25 process, (3) the second and third hexone cycle process wastes from aluminum fuels, and (4) first-cycle STR process wastes from processing of zirconium fuels with hydrofluoric acid. Exposure periods of the samples varied from 2.7 to 7 years. Corrosion specimens consisted of seamless and welded hoops, weld tabs, and sections of welded pipe. The hoops were prepared at the ICPP from sheet material that was turned into open-seam tubes by forming around a mandrel, leaving a $\frac{1}{8}$-in. opening.

Table IV-2 SUMMARY OF CORROSION IN ICPP WASTE-STORAGE TANKS[21]

Type of waste	Test coupon alloy,*	Tank capacity, gal	Max. exposure of coupons, years	Max. surface corrosion rate, mils/month
Acid-deficient $Al(NO_3)_3$ (1st cycle, hexone 25 process)	S.S. 348	300,000	7	1×10^{-3}
$Al(NO_3)_3$-HNO_3 (1st cycle, TBP-25 process)	S.S. 304L	300,000	2.7	1×10^{-2}
Aluminum (2d and 3d cycle, hexone 25 process)	S.S. 304L	300,000	2.7	6×10^{-3}
Zirconium-aluminum-HF (1st cycle, STR process)	S.S. 316L	30,000	5	1×10^{-2}

*The coupon was the same alloy as the construction material of the tank.

The open ends were then welded. This method of fabrication resulted in high retained stress levels.

The results of the evaluations are shown in Table IV-2. None of the exposed specimens in the first, second, and fourth types of waste were found to undergo any form of localized attack, including effects due to stress levels. However, some of the specimens exposed to the third type of process waste suffered from a rather heavy etch with shallow, 5-mil-deep pits. In addition, most of the original machine markings were corroded away. The author concludes that the general corrosion rates observed are too low to allow a significant estimate of the vessel life and that no evidence is now available suggestive of any type of corrosion failure of these vessels in the next 10-year period. Continued surveillance of test specimens in these vessels is planned.

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Section

V

Reactor Fuel Processing

Production of Uranium, Thorium, Plutonium, and Their Compounds

Recovery of Uranium from Ores

Chemical Processing of Uranium Ores

In a detailed review of the chemical processing of uranium ores, Pinkney, Lurie, and Van Zyl[1] have described methods for the physical concentration of uranium ores and have outlined the main steps in the extraction of uranium from ores. The chemistry and the technology of the processes are discussed. Three typical uranium-ore processing plants are described, and details of their respective process flow sheets are given.

Jodra and Josa[2] have published a monograph on the processing of uranium ores for the production of uranium concentrates. Specific details are presented on the leaching of the ores and the recovery of uranium from the leach solutions by direct precipitation, by ion exchange, and by organic solvent extraction.

Precipitation of Ammonium Uranates

In the processing of purified uranium solutions, uranium may be recovered by precipitation of ammonium diuranate. Vuillemey[3] has observed that the treatment of uranyl nitrate solutions with stoichiometric quantities of ammonia leads to nearly complete precipitation of the uranium; less than 1 mg of uranium per liter is left in solution. The precipitation of uranium from sulfate solutions by the addition of ammonia has been described by Deptula.[4] Proper adjustment of the *p*H of the solution during ammonia addition can lead to a readily filterable precipitate that leaves 2 mg of uranium per liter in the filtrate.

In a comprehensive study of the ammonium uranates, Cordfunke[5] has found that ammonium diuranate having the composition $(NH_4)_2U_2O_7$ is not obtained from aqueous solutions, even in the presence of a large excess of ammonia. Four compounds apparently can be prepared by the addition of ammonia to a uranyl nitrate solution; the composition of the compound obtained depends mainly on the *p*H of the solution and the quantity of ammonia present. From the results of chemical and X-ray analyses, the formulas of the four compounds have been tentatively established as $UO_3 \cdot 2H_2O$, $3UO_3 \cdot NH_3 \cdot 5H_2O$, $2UO_3 \cdot NH_3 \cdot 3H_2O$, and $3UO_3 \cdot 2NH_3 \cdot 4H_2O$.

The homogeneous precipitation of uranium with urea from uranyl nitrate solutions has been suggested as an alternative to the ammonium diuranate process.[6] The nature of the uranium precipitation products obtained from uranyl nitrate solutions containing urea has been extensively studied by Dembinski and Deptula.[7] Analyses showed that the products precipitated from solutions of high urea concentration have compositions approximating the compound $UO_3 \cdot 2CO(NH_2)_2 \cdot H_2O$. This compound is unstable in alkaline media. When a large excess of ammonia is present, the compound undergoes further reaction to form ammonium polyuranate containing only small amounts of urea. Similar behavior was observed in solutions of sodium or potassium hydroxide; the sodium and potassium polyuranates formed did not contain urea.

Production of Uranium Dioxide

Electrolytic Reduction of Uranyl Chloride

The process of electrodepositing coarse crystalline uranium dioxide from a fused-chloride electrolyte has been studied for application to the preparation of crystalline uranium dioxide

as a power-reactor fuel and the production of uranium from ore concentrates. Each of these applications is based on the fact that crystalline uranium dioxide can be prepared by the reduction of uranyl chloride dissolved in molten chloride salts.

The electrolyte is prepared by the direct chlorination of uranium oxides with chlorine gas in a molten chloride salt at 700°C. Uranium dioxide, U_3O_8, and uranium trioxide are all suitable feed materials. In molten chloride salt systems, the rate of dissolution of uranium dioxide by chlorine gas is low. Nonstoichiometric uranium dioxide having an oxygen-to-uranium ratio greater than 2.01 dissolves slightly faster, and U_3O_8 dissolves at a still higher rate. However, all these dissolution rates are considered low for process application. Lambert and Braun[8] have investigated the factors that appear to affect the dissolution of uranium oxides in molten chloride salts and have observed that the rate of oxidation of uranium dioxide to uranyl chloride is dependent on the concentration of uranyl chloride in the melt. This phenomenon appears to be due to the presence of UO_2^{2+} ions in the melt, and these ions may catalyze the oxidation of uranium dioxide through the formation of UO_2^{+} intermediate ions. As a result of this observation, several agents were evaluated with respect to their catalytic effect on the oxidation of uranium dioxide by chlorine in fused salts. It was found that the presence of 0.5 mole % iron (3+), copper (2+), or thallium (3+) markedly increased the dissolution rate of uranium dioxide. The catalytic effect of thallous chloride (TlCl) on the dissolution of uranium oxides in $ZnCl_2$-KCl fused salt is shown in Table V-1. The thallous chloride has a pronounced influence on the dissolution rate of uranium dioxide. Since oxidation is not involved in the dissolution of uranium trioxide, no effect of the catalyst is expected. Similarly, only a slight effect on dissolution of U_3O_8 was observed.

Table V-1 CATALYTIC DISSOLUTIONS OF URANIUM OXIDE POWDERS IN $ZnCl_2$-KCl FUSED SALT

[Conditions: Fused-Salt System, $ZnCl_2$-KCl (1 : 1 Mole Ratio); Temperature, 300°C; Sparge Gas, Chlorine]

Thallous chloride concentration, mole %	Rate of dissolution, mg of U per 10-min interval		
	UO_2	U_3O_8	UO_3
0	<3	27	40
1	113	93	40
3	560	260	40

At Hanford Atomic Products Operation (HAPO),[9,10] the electrolytic preparation of uranium dioxide has been investigated as a method for preparing uranium dioxide for direct use as a reactor fuel. To be suitable for use in a reactor, uranium dioxide should have a large crystal size, high density, and an oxygen-to-uranium ratio of less than 2.015. Several fused-salt systems were investigated as possible media for the deposition of uranium dioxide crystals. The only practical fused-salt systems found for the growth of large uranium dioxide crystals were LiCl-KCl (m.p. 460°C) and $PbCl_2$–2.5 KCl (m.p. 580°C). Pilot-plant tests at HAPO have been carried out in vessels and auxiliary equipment (Fig. V-1) of fused silica because no satisfactory metallic construction material has yet been developed. Based on pilot-plant runs and laboratory work, the following conclusions may be drawn:

1. The uranium oxide feed must be completely dissolved during the chlorination step to ensure production of reactor-grade uranium dioxide.
2. The presence of hydroxide or oxide impurities in the melt increased the tendency for crystal branching on the uranium dioxide deposit. The resulting branched crystals exhibited a high oxygen-to-uranium ratio, which suggested that branching may have been caused by the reduction of $U_3O_8^{2+}$ ions at the cathode. Removal of oxide and hydroxide constituents from the melt may be accomplished by providing a continuous atmosphere of HCl or Cl_2 over the melt and by sparging the bath with the same gases.
3. An initial uranium concentration in the melt of approximately 30 wt.% was necessary for the production of large uranium dioxide crystals. When the concentration of uranium was below 10 wt.%, there was a marked tendency toward crystal branching.
4. The optimum temperature range for the growth of large uranium dioxide crystals is 500 to 550°C. At temperatures above 550°C, the rates of competing reactions, such as the thermal decomposition of uranyl chloride and the dissolution of the uranium dioxide deposit by chlorine, increased, thereby making the proper conditions for the electrodeposition difficult to maintain.

Polycrystalline cylinders of uranium dioxide greater than 0.5 in. in diameter and 3 in. long

have been grown by electrodeposition from molten-salt solutions of uranyl chloride onto ¼- and ⅛-in.-diameter graphite electrodes.[11] Several rods of uranium dioxide which were large enough to be machined into 0.5-in.-diameter segments were prepared by electrolysis from a KCl-LiCl melt at 500°C. The electrolytic uranium dioxide deposits had densities up to 99% of theoretical and were composed of radially oriented columnar grains, which were quite free from voids. The deposits showed impurity levels of less than 50 ppm each of lithium and potassium and about 200 ppm chloride.

Of major concern in the production of electrolytic uranium dioxide is the fact that a uranium oxide product containing an oxygen-to-uranium ratio greater than 2 has frequently been observed. Wilks[12] has published the results of an investigation of the mechanism of the electrolytic reaction and discusses possible

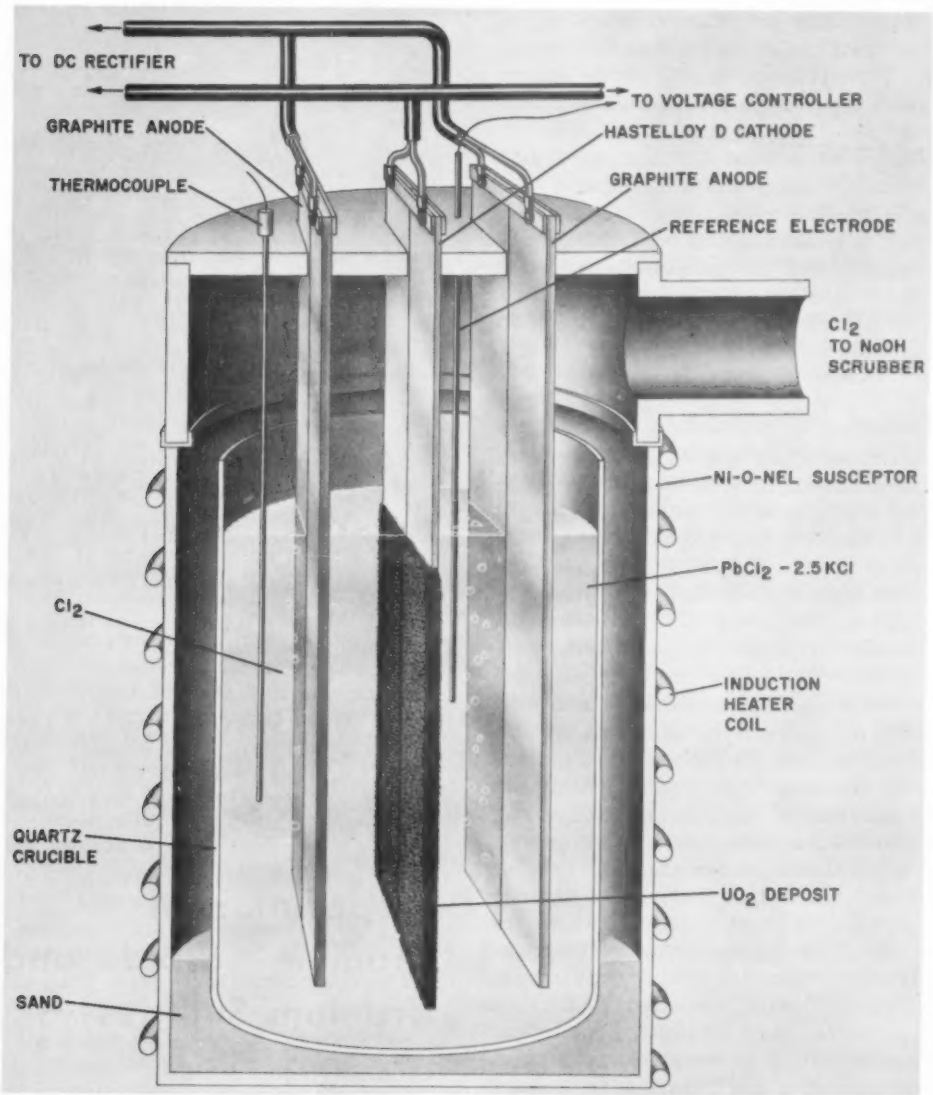

Fig. V-1 Electrolytic UO_2 pilot unit.[10]

reasons for the formation of U_4O_9 and UO_{2+x} crystals at the cathode. It was observed that the products at the electrodes do not correspond to the deposition of UO_2^{2+} and Cl^- ions only. Details of this study were discussed in a previous Review.[13]

Refined measurements[14] of capacitance as a function of potential have shown that the electroreduction of uranyl chloride to uranium dioxide in the sodium chloride–potassium chloride system does not proceed by a direct two-electron transfer. Data indicate that a soluble U(V) species exists as an intermediate in the reduction. Two reactions appear to occur: (1) $UO_2^{2+} + e^- \rightarrow UO_2^+$ and (2) $UO_2^+ + e^- \rightarrow UO_2(s)$. The capacitance-voltage plots show two peaks. The first is a symmetric peak that does not change in potential with a change in uranyl chloride concentration and is indicative of a reaction in which a soluble product is formed. The second is an asymmetric peak, the form of which indicates that the potential is dependent upon concentration in a fashion that denotes a one-electron exchange and the formation of an insoluble product.

Oxidation of Uranium Dioxide

The uranium-oxygen system is highly complex. The existence of at least five thermodynamically stable uranium oxides (UO_2, U_4O_9, U_3O_7, U_3O_8, and UO_3) has been definitely proved, and several additional oxides have been reported. The system is further complicated by polymorphism, formation of solid solutions, and metastability. Thus the mechanisms governing oxidation processes are not readily defined in this system. A considerable amount of information on the thermodynamic data for uranium oxides has been published in the Proceedings of the Symposium on Thermodynamics of Nuclear Materials.[15] Westrum and Groenvold[15a] have critically reviewed the existing experimental thermal and thermochemical data on uranium oxides. Low-temperature heat-capacity studies are described which have led to the understanding of the relation between the metastable uranium oxides and U_3O_7, U_4O_9, and U_3O_8. Aukrust et al.[15b] have measured equilibrium oxygen pressures over nonstoichiometric uranium dioxide (UO_{2+x}) at temperatures between 1100 and 1400°C. From these studies, a model for the defect structure in UO_{2+x} is suggested. Thermodynamic data have been obtained for oxides of composition between $UO_{2.01}$ and $UO_{2.6}$ by galvanic cell measurements between 500 and 1060°C by Markin et al.[15c,16] at Harwell. Roberts and Walter,[17] also at Harwell, have measured the pressure of oxygen in equilibrium with uranium oxides in the composition range $UO_{2.09}$ to $UO_{2.4}$ at temperatures of 1000 to 1450°C. It is now generally accepted that the phases which are stable above 600°C are: UO_2; a nonstoichiometric range UO_{2+x}, which is related to UO_2 by the inclusion of interstitial oxygen in the fluorite type lattice; U_4O_9, a cubic or pseudocubic phase, which is also related to UO_2 by the inclusion of interstitial oxygen; and U_3O_{8-z}, an orthorhombic phase of lower density than UO_2, and which is related in structure to U_3O_8.

Scott and Harrison[18] have studied the oxidation behavior of uranium dioxide powder in air at temperatures up to 800°C. They observed that powders of high surface area (>1 m^2/g) oxidize in a two-step process: first, to a tetragonal phase of composition $UO_{2.35}$ (tentatively identified as U_3O_7), and, then, to U_3O_8. The rate of oxidation for the U_3O_7 to U_3O_8 reaction is approximately four times greater than the rate of oxidation for the UO_2 to U_3O_7 reaction. The oxidation of uranium dioxide to U_3O_7 is apparently controlled by the diffusion of oxygen; this is followed by a process of nucleation and growth to U_3O_8. An activation energy of 19.1 kcal was derived for the $UO_2 \rightarrow U_3O_7$ oxidation step. Uranium dioxide of low surface area (<0.05 m^2/g) exhibited only a single-stage oxidation to U_3O_8.

Mukaibo et al.[15d] have determined the enthalpy change in the two-step oxidation of uranium dioxide to U_3O_8. The heat of reaction for $UO_2 + \frac{1}{6}O_2 \rightarrow \frac{1}{3}U_3O_7$ was -12.7 ± 0.8 kcal/mole at 230°C and for $\frac{1}{3}U_3O_7 + \frac{1}{6}O_2 \rightarrow \frac{1}{3}U_3O_8$ was -10.8 ± 0.7 kcal/mole at 380°C. The heat of formation, ΔH_f°, for U_3O_7 was estimated as -815.7 ± 2.4 kcal/mole.

Preparation of Uranium Carbide and Uranium Sulfides

Uranium Monocarbide

By comparison with other refractory compounds of uranium, uranium monocarbide is

particularly attractive as a nuclear fuel because of its high uranium density, high thermal conductivity, low parasitic neutron capture, and good irradiation resistance at high temperatures. Dense uranium monocarbide appears to be well suited for use in sodium- and organic-cooled reactors.

Among the most promising methods for preparing uranium monocarbide appears to be the reaction between uranium metal and carbon. Sato et al.[19] have described the preparation of single-phase uranium monocarbide by the solid-solid reaction of hydrided uranium metal and carbon at a temperature of 1100°C. The reaction mixture was prepared by blending uranium hydride with a stoichiometric quantity of finely ground graphite. After the mixture was heated at 450°C to decompose the hydride, the final reaction was carried out in a vacuum at 1100°C. Higher carbides, such as uranium dicarbide or uranium sesquicarbide, were not found in the monocarbide products. It was concluded that below 1000°C only uranium monocarbide can be obtained from the reaction of uranium hydride with carbon. This observation was substantiated in a series of tests in which uranium monocarbide was mixed with powdered carbon and heated to temperatures in excess of 1100°C. The presence of uranium dicarbide was observed only in preparations carried out at temperatures above 1300°C, whereas uranium sesquicarbide required temperatures in excess of 1500°C. In the preparation of uranium dicarbide by the reaction of uranium monocarbide with carbon, it was found that a temperature in excess of 1800°C was required to produce a single-phase product.

High-quality uranium monocarbide has also been prepared by the direct reaction of uranium dioxide and elemental carbon at high temperatures (1500 to 1750°C). In the method developed at The Carborundum Company,[20] uranium dioxide and carbon are blended, cold pressed without binder into pellets, and reacted at 1600°C in a vacuum furnace. The reaction conditions have been studied at several temperature levels between 1450 and 1750°C. It was concluded from these tests that there is no advantage in conducting the reaction at temperatures higher than 1600°C. The uranium monocarbide products have been fabricated into sintered pellets having approximately 90% of the theoretical density. The procedure adopted for pellet fabrication was to grind the uranium monocarbide product to an average particle size of 1 to 2 μ, press the powder at 16,500 psi in the presence of a binder, and sinter the compacts in a vacuum furnace at 1940°C.

A series of tests was performed[20] to evaluate the effect of certain additives on the sintered density of uranium monocarbide. The presence of 5% UC_2, 5% UO_2, and 10% UN showed no effect on the final density of sintered compacts. Nickel metal powder in concentrations ranging from 0.1 to 0.2 wt.%, however, was observed to aid in densification of uranium monocarbide by promoting grain growth during sintering. The presence of nickel metal also promotes the formation of uranium sesquicarbide (U_2C_3) when uranium monocarbide compacts are sintered at 1525°C. Metallographic examination indicated that specimens sintered at 1525°C in the presence of 0.1 wt.% nickel usually contained 15% of a second phase believed to be U_2C_3.

Properties of Uranium Carbides

Since the carbides of uranium are becoming of increasing technical importance for the development of nuclear reactors, knowledge of their thermodynamic and physical properties is of practical interest. Huber and Holley[21] have reviewed the present state of knowledge of the thermodynamic properties of the actinide carbides and have reported recent measurements on the heats of formation of several actinide carbides. The heats of formation, free energies of formation, entropies of formation, and absolute entropies of several actinide carbides at 298°K are presented in Table V-2. Vozzella et al.[22] have reported the results of a study on the thermal stability of uranium monocarbide and have calculated the heat of vaporization of uranium monocarbide at 298°K to be 324.6 ± 2 kcal/mole. Also, they have obtained a value of

Table V-2 THERMODYNAMIC FUNCTIONS AT 298°K FOR THE FORMATION OF THE ACTINIDE CARBIDES[21]

(Figures in Parentheses Are Estimates)

Compound	$\Delta H°$, kcal/mole	$\Delta F°$, kcal/mole	$\Delta S°$, entropy units	$S°$, entropy units
ThC	−7 ± 6	−6.4 ± 6	(−2)	(12)
ThC_2	(−31)	(−32.5)	(+4)	(19.6)
UC	−20.8 ± 0.9	−20.1 ± 1.0	2.1 ± 0.5	11.3 ± 0.5
U_2C_3	−49 ± 4	−48 ± 5	−3	25
$UC_{1.88}$	−18 ± 4	−19 ± 5	(4)	(19)
$PuC_{0.77}$	3.7 ± 3.1	2.5 ± 4	(4)	(17)
Pu_2C_3	−1.7	(0.8)	(−3)	(25)

the standard heat of formation for $UC_{1.1}$ at 298°K which is -19.4 ± 2.0 kcal/mole.

Uranium Sulfides

The desire for greater efficiency in reactor operation has led to the search for nuclear fuels that can withstand high burnups at increasingly higher operating temperatures. A material that appears attractive as a fuel is uranium monosulfide which has a uranium density comparable to that of uranium dioxide and a cubic structure that is stable to its melting point of 2460°C. Shalek[23] at Argonne National Laboratory (ANL) has prepared high-purity uranium monosulfide (US) by a two-step method. In the first step, uranium-metal turnings are hydrided, the hydride is decomposed to give a fine powder, and the powdered metal is reacted at 400 to 550°C with a measured volume of hydrogen sulfide to give a product containing a mixture of uranium disulfide (US_2) and uranium metal. In the second step the mixture is blended and heated to 1800°C in a vacuum furnace to produce the uranium monosulfide. By means of this procedure, uranium monosulfide containing up to 99.9 wt.% US phase has been prepared.[24]

Development work has begun[25] on a method by which uranium monosulfide can be synthesized directly. The process involves bubbling a hydrogen sulfide stream through an alkali melt containing uranium in solution. Initial tests are being made with uranium tetrafluoride dissolved in a fused-salt bath composed of 50 mole % NaCl–50 mole % KCl. In an effort to minimize oxygen contamination, hydrogen chloride gas is bubbled through the molten salt to remove occluded moisture. The use of a fused-salt media for the preparation of actinide monosulfides has been described by Didchenko and Litz.[26] In this work the monosulfide is produced by electrolysis of uranium tetrachloride in the presence of sodium sulfide in a fused chloride system.

Powdered uranium monosulfide has been sintered to densities up to 92% of theoretical.[23,24] It was observed that rapid sintering of uranium monosulfide takes place in the presence of 1 wt.% or more of UOS which forms a liquid eutectic with the monosulfide at 1750°C.

Groenvold et al.[27] have described methods for the preparation of uranium sulfides in the range of composition $US_{1.5}$ to $US_{3.1}$. Several species within this composition range have been characterized and their physical properties measured.

Production of Uranium Metal

Electrolytic Reduction of Uranium Dioxide

High-quality uranium metal has been produced at Mallinckrodt Chemical Works from uranium dioxide by fused-salt electrolysis using a consumable anode that contains a uranium dioxide–carbon mixture.[28] The reduction cell consists of a cylindrical graphite crucible that serves both as the cathode of the cell and as a container for the molten electrolyte and molten metal. Details and descriptions of the process have appeared in previous Reviews.[29,30]

It has been observed[28] that operation of the electrolytic cells for extended periods generally leads to the formation of a layer of black material at the electrolyte surface. This layer has an electrical conductivity that is sufficiently high to lead eventually to short-circuiting of the cell. Analyses of the material have shown the presence of carbon and graphite particles. A carbon dioxide purge over the electrolyte has been effective in controlling the formation of the layer by oxidation of the carbon, but its use leads to undesirable attack on the graphite parts of the cell.

It appears that the conducting nature of the layer is provided by a bond of uranium metal or uranium carbide between the carbon particles. If this bond is not formed, only loose, poorly conducting carbon particles accumulate on the electrolyte surface. Considerable success has been achieved in regulating the formation of the conducting material by changing the geometry of the electrolytic cell in such a manner that the current density at the layer is maintained at a minimum value, thereby eliminating the formation of uranium metal at the surface. The cathode current density may be kept low by making the anode-to-cathode distance at the surface of the electrolyte greater than that below the surface. Several tests[28] have shown that anode-to-cathode distances of $2\frac{1}{4}$ in. at the surface and $\frac{3}{8}$ in. at a point below the surface have been effective in preventing the layer formation in laboratory-scale cells.

A major factor in limiting the anode current density, and hence the throughput of a cell of a

particular size, is the anode effect. This effect is observed as a sudden drop in current and increase in voltage to the cell and appears to be caused by an insulating barrier or gas film on the surface of the anode. A series of tests was performed[31] to determine the maximum anode current density that can be maintained without the anode effect. The electrolyte was composed of an equimolar mixture of barium fluoride and lithium fluoride with from 10 to 20 wt.% uranium tetrafluoride. The maximum anode current density that can be maintained without producing the anode effect varied from 0.65 amp/cm^2 with 10 wt.% uranium tetrafluoride in the electrolyte to 1.4 amp/cm^2 with 20 wt.% uranium tetrafluoride in the electrolyte. The presence of uranium dioxide dissolved in the electrolyte had a noticeable effect on the maximum anode current density. The addition of 0.33 wt.% uranium dioxide to the electrolyte increased the maximum anode current density of an electrolyte containing 10 wt.% uranium tetrafluoride from 0.68 amp/cm^2 to 1.30 amp/cm^2. Further additions of uranium dioxide had no effect on the anodic current density.

In order to provide information necessary for the calculation of the power requirements for the electrolytic cell and heat generation during cell operation, the electrical conductivity of the molten BaF_2–LiF electrolyte has been measured.[32] The specific conductivities at 1150°C varied from 3.5 (ohm-cm)$^{-1}$ to greater than 4.7 (ohm-cm)$^{-1}$, depending on the lithium fluoride to barium fluoride mole ratio. The conductivity increased with increasing lithium fluoride to barium fluoride mole ratio. The effect of varying uranium tetrafluoride concentration was not clear.

Bomb Reduction of Uranium Tetrafluoride

Massive uranium metal is produced at the National Lead Company of Ohio (NLCO) by a thermite reaction in which uranium tetrafluoride (green salt) is reduced by granular magnesium in a closed steel vessel lined with ground magnesium fluoride slag. In present practice a loose blend of green salt and magnesium is packed into the vessel, which is then capped and heated inside an electric resistance furnace until the reaction occurs. A program has been initiated at NLCO to evaluate on a production scale the replacing of the loose uranium tetrafluoride–magnesium charge with briquettes of the same composition. Previous work, reported in *Reactor Fuel Processing*,[33] indicated that briquettes fabricated at a pressure of 16 tsi showed a significant increase in derby yields and an improved derby quality over unbriquetted charges.

In recent studies[34] it was determined that a minimum pressure of 8 tsi was required to produce good-quality briquettes of uranium tetrafluoride–magnesium. Both dehydrated uranium tetrafluoride (Winlo process[35]) and uranium tetrafluoride produced from hydrofluorinated uranium dioxide produced briquettes with good physical strength at pressures of 8 tsi or higher. It was observed[34] that holding the briquettes under pressure in the press for a dwell period of 10 sec increased the density of the briquettes by an amount equivalent to that obtained by increasing the pressure an additional 2 tsi without such a dwell period. An increase of the briquetting pressure from 8 to 16 tsi increased the briquette density less than 5%. When, in addition to physical strength, the chemical reduction characteristics of the briquettes were taken into consideration, the optimum briquetting pressure was indicated to be 10 tsi with a 10-sec dwell period.

Test reductions were performed with briquettes containing three magnesium excess levels: 0.6, 2.1, and 3.6% excess magnesium. In general, the briquettes containing 3.6% excess magnesium gave better results with both types of green salt tested. Derby yields from briquettes containing uranium tetrafluoride from hydrofluorinated uranium dioxide averaged 99.6%. Exceptionally clean derbies were produced with both types of green salt at the 3.6% level of excess magnesium.

The adoption of uranium tetrafluoride–magnesium briquetting as a production practice would have several advantages in addition to the production of clean derbies at high yields: (1) elimination of chemical processing of reduction residues which would provide a marked reduction in costs, (2) elimination of magnesium fluoride slag from the recasting operation which would improve ingot quality, and (3) better accountability of materials resulting from the more uniform reduction results.

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